

# GAS PHASE STUDIES OF THE NEGATIVE ION CHEMISTRY OF SILICON

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## 1. GENERAL INTRODUCTION

The importance of intermediates in organic chemistry has encouraged organosilicon chemists to pursue studies of analogous silicon-containing species. Only very recently have silenes ( $R_2Si=CR'_2$ ) and silylenes ( $R_2Si:$ ), which are olefin and carbene analogues, been isolated either at room temperature or in low temperature matrices in cases where extremely bulky substituents impart kinetic stability to otherwise highly reactive intermediates.<sup>1-3</sup> Attempts to generate silicon cations (silicenium cations) ( $R_3Si^+$ ) in solution have been made for some forty years with controversy still surrounding their existence.<sup>4-6</sup> Silicon anion equivalents have been known in solution for some time. Such species are useful synthetic reagents, but generally have complex organometallic structures associated with their metal counterions and the solvents required in their preparation.<sup>3,6,7</sup> Other ionic silicon species, namely pentacoordinate cations and anions, have a complex relationship to their carbon analogues since carbon is not generally pentacoordinate. Pentacoordinate silicon anions (siliconates) ( $R_5Si^-$ ) were long ago proposed as intermediates in nucleophilic substitution reactions in solution,<sup>8</sup> but only recently have such solution species become generally accepted and in many cases easily prepared.<sup>9-13</sup>

The situation for such silicon species in the gas phase is strikingly different. Both silenes and silylenes have been studied in detail by gas phase methods in work that has been thoroughly reviewed.<sup>1,3,14</sup> Silicon cations and anions (both tri and pentavalent) are also readily prepared and studied.<sup>6,15-17</sup> Two recent reviews of gas phase silicon ion chemistry bear witness to the importance and popularity of silicon ion chemistry, although these tend to concentrate more on positive than negative ion chemistry.<sup>18,19</sup>

The main purpose of this review is to emphasize to silicon chemists the importance of negative ion gas phase chemistry. Since our review of gas phase negative ion silicon work in 1987,<sup>15</sup> many additional silicon studies have been undertaken. We will concentrate on these newer aspects of silicon chemistry in this chapter. Our own gas phase studies have been carried out using flowing afterglow techniques and these studies will be the focus of this chapter. After a brief introduction of the experimental tools we use (Section 2), we will consider some of the thermochemical properties of silicon-containing neutrals which can be determined from negative ion-molecule chemistry in gas phase studies (Section 3). In presenting some of the relationships between

negative ion chemistry and the thermochemistry of neutral and ionic species, the importance of negative ion studies for silicon chemists will be emphasized. Finally, a number of reaction studies of silicon-containing compounds will be considered (Section 4). These will enable us to explore the reactivity relationships, reaction mechanisms, and properties of silicon compounds which have been studied under negative ion conditions by gas phase techniques. Although we will emphasize our own work in this chapter, reference will be made to several workers who have made important contributions to negative ion gas phase silicon chemistry. They include John Bowie, John Brauman, Terry McMahon, John Sheldon, and Bob Squires.

## 2. PRIMER ON FLOWING AFTERGLOW TECHNIQUES

Much of the chemistry to be described occurs because ion-molecule reactions often take place very rapidly with bimolecular rate constants as high as  $10^{12}$  L mole<sup>-1</sup> s<sup>-1</sup> ( $2 \times 10^{-9}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>).<sup>15</sup> Such reactivity is governed by ion-dipole attractive forces which are typically  $\sim 20$  kcal/mol. This ion-molecule attraction usually results in a relatively long-lived complex ( $10^{-7}$  to  $10^{-12}$  s). Since this complex (adduct) is formed with considerable internal energy, it must be stabilized by a collision with a third body in order to survive. If it is too short-lived to dissipate its internal energy by such a collision, it will dissociate to reactants and not be detected. Instead, it will either dissociate to reactants or yield other products. Adducts are more often detected in the gas phase with high pressure [e.g., flowing afterglow (FA)] than low pressure (e.g., ion cyclotron resonance) mass spectroscopic techniques since the higher pressures make stabilizing collisions more frequent.

Two different flowing afterglow systems have been used in our work. The conventional flowing afterglow apparatus (Figure 1), which we used initially, consists of an ionization region where simple anions are produced by direct electron impact ionization, a reaction region where anions react with neutral molecules which can be introduced either through a fixed or movable inlet, and a detection region where ions are sampled and mass analyzed.<sup>20</sup> A buffer gas (usually He) at fairly high pressures ( $\sim 0.5$  Torr) is pumped through the system carrying ions from the ionization region down a stainless steel flow tube to react with neutrals. The ions produced by direct ionization undergo

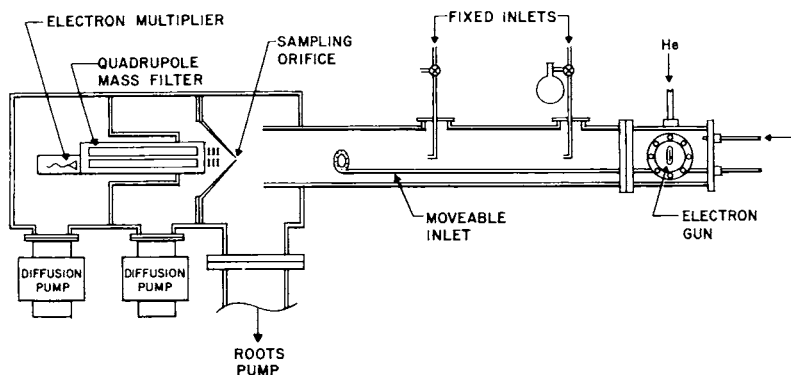
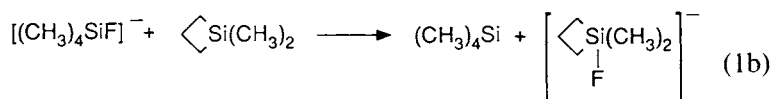
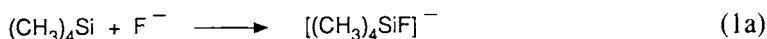


Figure 1

numerous collisions with the buffer gas ensuring that thermal equilibration occurs. In the reaction region, sequential anion-molecule reactions can be carried out at several neutral addition inlets. Finally, the anions are sampled through an orifice, separated by a quadrupole mass filter, and detected by an electron multiplier. In a typical example,  $F^-$  is produced by electron impact of  $NF_3$  and swept down the flow tube to the reaction region where it is allowed to react with  $(CH_3)_4Si$  to produce  $[(CH_3)_4SiF]^-$  (eq. 1a). This siliconate adduct can be cooled by collision with He and allowed to react further down the flow tube with silacyclobutane. Fluoride transfer occurs to give a new siliconate anion,  $[(CH_2)_3Si(CH_3)_2F]^-$ , and tetramethylsilane (eq. 1b). In a typi-



cal FA experiment, only the ionic products are detected by mass analysis; neutral products are inferred from our knowledge of the reactants, the anionic products, and the likely mechanistic pathways followed.

Our more recent flowing afterglow studies have been carried out using the tandem Flowing Afterglow Selected Ion Flow Tube (FA-SIFT) technique.<sup>21</sup> A diagrammatic representation of such an apparatus is shown in Figure 2. The tandem FA-SIFT is a significant advance

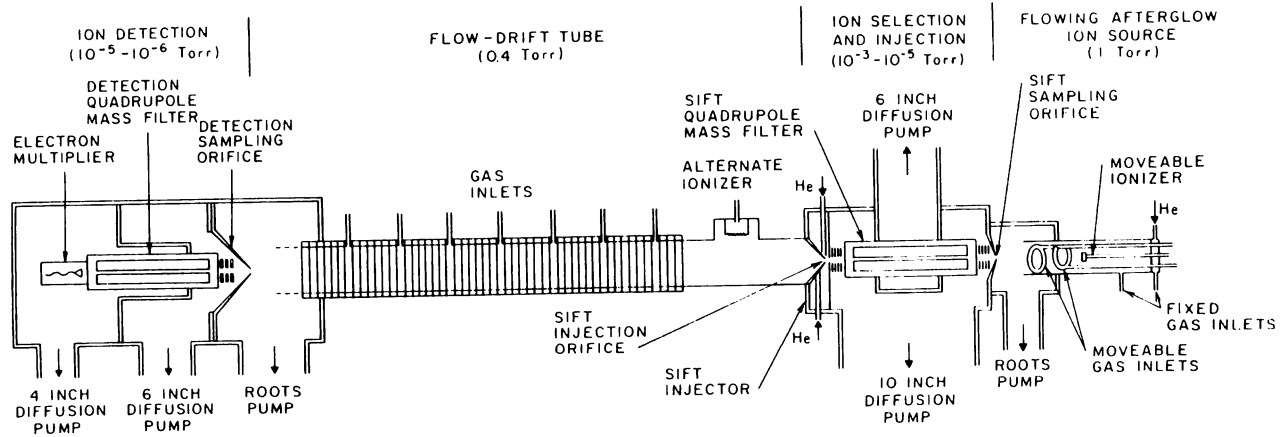


Figure 2

over the conventional instrument since it not only incorporates all the conventional features, but allows a cleaner production of ions for study in a second flow tube. In this new apparatus, complex mixtures of ions can be produced in a flowing afterglow ion source from which an anion can be mass selected and injected into a second flow tube. The utility of the tandem FA-SIFT becomes clear when we recognize that electron impact of methylsilane gives a complex product mixture of some 20 anions. Under conventional flowing afterglow conditions, such a mixture could not be studied, but using the tandem FA-SIFT, we have been able to select ions of a single mass-to-charge ratio and inject them into the second flow tube for further study. To inject ions from the low pressure region of the SIFT quadrupole ( $10^{-6}$  torr) into the higher pressure regime of the second flow tube, an electrical potential must be applied. This potential imparts kinetic energy to the ions, energy which is generally removed by multiple collisions with the buffer gas. If this potential is made sufficiently high, however, ions sometimes undergo collision-induced dissociation (CID) to form new ions. Subsequently, in a field-free region, these resulting new ions undergo multiple collisions with buffer gas and are usually cooled to room temperature before being allowed to react with neutral reagents. In some cases, individual ions are produced so cleanly by CID that their chemistry can be explored.

### 3. PROPERTIES OF SILICON-CONTAINING NEUTRALS

#### 3.1. General Comments on Thermochemistry

Various thermochemical properties of neutral molecules are accessible from negative ion-molecule reaction studies.<sup>22</sup> In many cases, such properties are more easily obtained using ion-molecule chemistry than by other techniques. In this short section, we will outline in general terms some of the thermochemical cycles that have been used in negative ion gas phase silicon chemistry. In the following sections, specific examples of their application will be given.

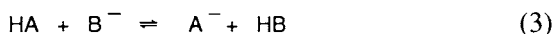
Equation 2<sup>22</sup> relates the gas phase acidity of HA ( $\Delta H_{\text{acid}}^{\circ}$ ), the bond dissociation energy (BDE) of H–A, the electron affinity (EA) of A, and the ionization potential (IP) of H:





Gas phase acidity measurements can often be combined using this thermochemical cycle to obtain the other thermochemical quantities (eq. 2).<sup>23</sup> Since the ionization potential of H is well known, this cycle can be used to obtain either BDE's or EA's. Examples where the  $\Delta H_{\text{acid}}^\circ$  and EA are known have yielded new BDE's, and examples where  $\Delta H_{\text{acid}}^\circ$  and BDE are known have given new EA's. The power of these approaches derives from the relative ease by which many acidities can be measured as well as the difficulty sometimes encountered of making direct EA and BDE measurements.

One way of measuring acidity is to determine the rate of the forward and reverse reaction between HA and a suitable base ( $B^-$ ) and thereby determine the equilibrium constant for the reaction (eq. 3). While



many gas phase acidities have been determined this way, the method is not applicable if either HA or HB is unavailable. Thus, if  $A^-$  is an anion that can be readily made in the gas phase, but its conjugate acid, HA, cannot be obtained, then the acidity of HA cannot be determined by equilibrium methods.

An alternative is the bracketing method<sup>22,23</sup> in which a series of reference acids (HB's in eq. 3) are allowed to react with  $A^-$ . Some transfer a proton giving HA; others do not. Assuming rapid proton transfer whenever it is exothermic, 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 difference in acidity between the closest reacting and non-reacting HB acids) can be obtained. Thus, although an equilibrium acidity measurement is preferred because it is usually more accurate, the bracketing method is the only choice when certain acids cannot otherwise be obtained. We will see examples of this for silicon-containing acids which, because of their high reactivity, cannot be made easily, even in the gas phase.

Acidity measurements can be linked to other thermochemical cycles to obtain additional important information on gas phase species. Sup-

pose, for example, that an anion,  $\text{HX}^-$ , can be prepared in the gas phase and: (1) the acidity of its conjugate acid,  $\text{H}_2\text{X}$ , can be measured; (2)  $\text{HX}^-$  undergoes reactions which transfer  $\text{H}^-$ ; and (3) the heat of formation of  $\text{X}$  is known. From eqs. 4 and 4a, which define the

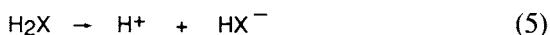


$$\underline{\text{HA}}(\text{X}) = \Delta H_f^\circ(\text{X}) + \Delta H_f^\circ(\text{H}^-) - \Delta H_f^\circ(\text{HX}^-) \quad (4a)$$

hydride affinity ( $\underline{\text{HA}}$ )<sup>24,25</sup> of  $\text{X}$ , we see that, if  $\underline{\text{HA}}(\text{X})$  and the heat of formation of  $\text{X}$  are known, then the heat of formation of  $\text{HX}^-$  is easily obtained since the heat of formation of  $\text{H}^-$  is accurately known (eq. 4b). Hydride affinities are often accessible to ion chemists by bracket-

$$\Delta H_f^\circ(\text{HX}^-) = + \Delta H_f^\circ(\text{X}) + \Delta H_f^\circ(\text{H}^-) - \underline{\text{HA}}(\text{X}) \quad (4b)$$

ing experiments involving the transfer of  $\text{H}^-$ . Thus, the condition placed on  $\text{HX}^-$  above, namely that it undergo  $\text{H}^-$  transfer reactions, serves to indicate that the  $\underline{\text{HA}}(\text{X})$  can be determined. By combining  $\Delta H_f^\circ(\text{HX}^-)$  and the acidity of  $\text{H}_2\text{X}$  (eqs. 5 and 5a), we see that the heat



$$\Delta H_f^\circ(\text{H}_2\text{X}) = \Delta H_f^\circ(\text{HX}^-) + \Delta H_f^\circ(\text{H}^+) - \Delta H_{\text{acid}}^\circ(\text{H}_2\text{X}) \quad (5a)$$

of formation of the conjugate acid,  $\text{H}_2\text{X}$ , can be determined since the heat of formation of  $\text{H}^+$  is well known.

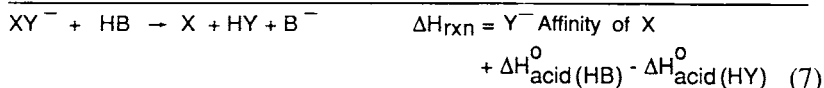
A final example of the importance of thermochemical cycles in gas phase chemistry supposes that a gas phase species,  $\text{XY}^-$ , reacts with a series of reference acids,  $\text{HB}$ , as shown in eq. 6. Here the reference



acids bracket the reaction. If both the acidities of  $\text{HB}$  and  $\text{HY}$  acids are known and the bracket can be narrowly determined, then the affinity of  $\text{Y}^-$  for  $\text{X}$  can be determined (eq. 7a). Such affinity measurements can







sometimes be made directly by gas phase equilibrium measurements, but the method just described can offer certain advantages, particularly when X is not easily obtained, but  $\text{XY}^-$  is.

### 3.2. Gas Phase Acidities of Silicon-Containing Compounds

Table 1 presents the gas phase acid strengths of a representative number of silicon-containing compounds arranged by silicon substitution pattern and compared with analogous carbon species.<sup>22,26-41</sup> [Note that acid strength increases with decreasing values of  $\Delta H_{\text{acid}}^{\circ}$ ]. The acidities have been arranged to emphasize two different substitution effects on silicon. The  $\alpha$ -effect illustrates how substitution patterns on silicon affect the acidity of a H bonded to silicon. The  $\beta$ -effect probes how different bonding situations at silicon and changing substitution patterns on silicon affect the acidity of an adjacent C—H, O—H, or N—H group.

For both the  $\alpha$ - and  $\beta$ -effect, silicon compounds tend to be more acidic than their carbon analogs. The difference can be extremely large as in the case of silane and methane (44 kcal/mol) or quite small as in the case of silacetone and acetone (7 kcal/mol). The thermochemical cycle illustrated in eq. 2 can often be used to give a clear picture of the dominating effects in a particular acidity comparison. For example, both the corresponding BDE's and EA's contribute to increase the acidity difference of  $\text{SiH}_4$  relative to methane (BDE of C—H is stronger by 15 kcal/mol than Si—H<sup>42</sup> and EA shows the silyl anion to be more stable to electron detachment than the carbanion by 30 kcal/mol).<sup>27</sup> We have shown that methyl  $\alpha$ -substitution is complex in alkanes with the first alkyl substitution (methane to ethane) decreasing C—H acid strength and each additional one increasing it.<sup>30</sup> This results from competing effects. Thus, the first methyl substitution inductively destabilizes the carbanion, but additional methyl substitutions stabilize carbanions as polarizability effects overcome inductive effects. This is not the case in the silicon series where the first methyl substitution (silane to methylsilane) gives a fairly large decrease in Si-H acid strength, but additional ones do not increase the acidity and, in fact, have essentially no effect.<sup>26,27</sup> The effect of an aromatic substituent is

**Table 1.** Acidities ( $\Delta H_{\text{acid}}^{\circ}$ ) of Representative Silicon and Carbon Compounds

<i>Silicon Compound</i>	$\Delta H_{\text{acid}}^{\circ}$ (kcal/mol)	<i>Carbon Analog</i>	$\Delta H_{\text{acid}}^{\circ}$ (kcal/mol)
<b><math>\alpha</math>- effect</b>			
$\text{SiH}_3\text{-}\underline{\text{H}}$	373 <sup>27</sup>	$\text{CH}_3\text{-}\underline{\text{H}}$	417 <sup>30</sup>
$\text{CH}_3\text{SiH}_2\text{-}\underline{\text{H}}$	378 <sup>27</sup> (383) <sup>26</sup> see (a)	$\text{CH}_3\text{CH}_2\text{-}\underline{\text{H}}$	420 <sup>30</sup>
$(\text{CH}_3)_2\text{SiH-}\underline{\text{H}}$	383 <sup>26</sup>	$(\text{CH}_3)_2\text{CH-}\underline{\text{H}}$	419 <sup>30</sup>
$(\text{CH}_3)_3\text{Si-}\underline{\text{H}}$	383 <sup>26,27</sup>	$(\text{CH}_3)_3\text{C-}\underline{\text{H}}$	413 <sup>30</sup>
$\text{C}_6\text{H}_5\text{SiH}_2\text{-}\underline{\text{H}}$	370 <sup>26,27</sup>	$\text{C}_6\text{H}_5\text{CH}_2\text{-}\underline{\text{H}}$	381 <sup>22</sup>
$\text{C}_6\text{H}_5(\text{CH}_3)\text{SiH-}\underline{\text{H}}$	374 <sup>27</sup>	$\text{C}_6\text{H}_5(\text{CH}_3)\text{CH-}\underline{\text{H}}$	380 <sup>22</sup>
$\text{HSi(=O)-}\underline{\text{H}}$	362 <sup>37</sup>	$\text{HC(=O)-}\underline{\text{H}}$	393 <sup>22</sup>
$\text{CH}_3\text{OSi(=O)-}\underline{\text{H}}$	362 <sup>34</sup>	$\text{CH}_3\text{OC(=O)-}\underline{\text{H}}$	—
<b><math>\beta</math>- effect</b>			
$\text{SiH}_3\text{CH}_2\text{-}\underline{\text{H}}$	388 <sup>26</sup>	$\text{H}_3\text{CCH}_2\text{-}\underline{\text{H}}$	420 <sup>30</sup>
$\text{CH}_3\text{SiH}_2\text{CH}_2\text{-}\underline{\text{H}}$	391 <sup>26</sup>	$\text{CH}_3\text{CH}_2\text{CH}_2\text{-}\underline{\text{H}}$	416 <sup>30</sup>
$(\text{CH}_3)_2\text{SiHCH}_2\text{-}\underline{\text{H}}$	391 <sup>26</sup>	$(\text{CH}_3)_2\text{CHCH}_2\text{-}\underline{\text{H}}$	413 <sup>30</sup>
$(\text{CH}_3)_3\text{SiCH}_2\text{-}\underline{\text{H}}$	391 <sup>28</sup>	$(\text{CH}_3)_3\text{CCH}_2\text{-}\underline{\text{H}}$	409 <sup>30</sup>
$\text{F}_3\text{SiCH}_2\text{-}\underline{\text{H}}$	367 <sup>31</sup>	$\text{F}_3\text{CCH}_2\text{-}\underline{\text{H}}$	—
$\text{F}_2(\text{CH}_3)\text{SiCH}_2\text{-}\underline{\text{H}}$	379 <sup>31</sup>	$\text{F}_2(\text{CH}_3)\text{CCH}_2\text{-}\underline{\text{H}}$	—
$\text{F}(\text{CH}_3)_2\text{SiCH}_2\text{-}\underline{\text{H}}$	387 <sup>31</sup>	$\text{F}(\text{CH}_3)_2\text{CCH}_2\text{-}\underline{\text{H}}$	—
$(\text{CH}_3)_3\text{SiNH-}\underline{\text{H}}$	379 <sup>32</sup>	$(\text{CH}_3)_3\text{CNH-}\underline{\text{H}}$	399 <sup>32</sup>
$(\text{CH}_3)_3\text{SiO-}\underline{\text{H}}$	359 <sup>33</sup>	$(\text{CH}_3)_3\text{CO-}\underline{\text{H}}$	374 <sup>22</sup>
$\text{CH}_3\text{Si(=O)CH}_2\text{-}\underline{\text{H}}$	362 <sup>34</sup>	$\text{CH}_3\text{C(=O)CH}_2\text{-}\underline{\text{H}}$	369 <sup>22</sup>
$\text{Si=CH-}\underline{\text{H}}$	360 <sup>38</sup>	$\text{HC=C-}\underline{\text{H}}$	378
$\text{CH}_2=\text{Si}(\text{CH}_3)\text{CH}_2\text{-}\underline{\text{H}}$	$\sim 374$ <sup>39</sup>	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{-}\underline{\text{H}}$	390
$\text{CH}_3\text{SiCH}_2\text{-}\underline{\text{H}}$	$\sim 379$ <sup>40</sup>	$\text{CH}_3\text{CCH}_2\text{-}\underline{\text{H}}$	—

(a) There is a discrepancy between these two reported values, one measured by bracketing<sup>26</sup>, the other by equilibrium measurements.<sup>27</sup> In the bracketing experiments,  $\text{CH}_3\text{SiH}_2^-$  was found to abstract a proton from methanol suggesting that the acidity value must be greater than 380 kcal/mol. In recent experiments done under far more suitable conditions, we have confirmed this observation.<sup>32</sup>

also dramatically different for silicon and carbon. Both  $\text{C}_6\text{H}_5\text{SiH}_3$  and  $\text{C}_6\text{H}_5(\text{CH}_3)\text{SiH}_2$  have nearly the same acidity as  $\text{SiH}_4$  while toluene and  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$  have acid strengths almost 40 kcal/mol greater than methane.<sup>26,27</sup> While both  $\text{SiH}_4$  and  $\text{C}_6\text{H}_5\text{SiH}_3$  have nearly identical BDE's and their radicals have similar EA's, a comparison of methane and toluene shows that both the BDE and EA strongly contribute to their large difference in acidity<sup>22,26,27</sup> with methane having a stronger C-H bond than toluene and  $\text{CH}_3^-$  being a far less stable anion than  $\text{C}_6\text{H}_5\text{CH}_2^-$ .

The effect of  $\beta$ -methyl substitution on C—H acidity is more regular for the alkanes with each  $\beta$ -methyl addition leading to an increase in acid strength.<sup>30,41</sup> Neopentane is some 11 kcal/mol more acidic than ethane. Here the dominating effect has been attributed to polarizability with each polarizable methyl addition leading to a greater stabilization of the carbanion.<sup>30,41</sup> Polarizability effects of this type are common in gas phase behavior<sup>23,43,44</sup> and were first carefully considered in pioneering studies by Brauman and Blair on the gas phase acidity of alcohols and amines.<sup>43,45</sup> In contrast to the acidities of alcohols measured in protic solvents, they discovered that incremental  $\beta$ -methyl substitution leads to monotonic increases in acid strength with *t*-butyl alcohol being more acidic than ethyl alcohol in the gas phase. The  $\beta$ -methyl substitution effect on silicon shows no such behavior (Table 1).<sup>26</sup> We see that C-H acidity in the series  $(\text{CH}_3)_n\text{Si}(\text{H})_{3-n}\text{CH}_2\text{—H}$  varies hardly at all and certainly does not show any monotonic increase with  $\beta$ -methyl substitution. We believe that these results are consistent with an interpretation that the two major competing substituent effects, inductive and polarizability, have about the same magnitude here. The polarizability effect which has an  $r^{-4}$  distance dependence is attenuated relative to the inductive effect ( $r^{-2}$ ) in the silicon versus alkane series because the critical distances are greater in the silicon series. The silicon data cannot be further refined because of experimental problems even though it would be important to have more accurate measures of the acidities in the silicon series. As we will see shortly,  $\beta$ -methyl substituent effects in silanols are the reverse of those of alcohols.

Silyl amines are more acidic than the corresponding silyl alkanes by about the same extent that ammonia (404 kcal/mol) is more acidic than methane (417 kcal/mol) indicating that there is no special effect with silicon substitution in amines [compare  $(\text{CH}_3)_3\text{SiNH}_2$  and  $(\text{CH}_3)_3\text{SiCH}_3$ ].<sup>28,32</sup> That is, a silyl substitution makes an amine N—H no more acidic relative to a corresponding C—H acid. As we have seen all along, however, a silyl substitution increases the acid strength, N—H in this case, when compared to a carbon substitution. That is, the N—H acidity of  $(\text{CH}_3)_3\text{SiNH}_2$  is about 20 kcal/mol greater than that of  $(\text{CH}_3)_3\text{CNH}_2$ .

Silyl alcohols (silanols) exhibit similar behavior to the amines. Water is some 26 kcal/mol more acidic than methane and  $(\text{CH}_3)_3\text{SiOH}$  is 32 kcal/mol more acidic than  $(\text{CH}_3)_3\text{SiCH}_3$ . Furthermore, trimethylsilanol is 15 kcal/mol more acidic than *t*-butyl alcohol. Although our acidity determinations are often cruder than we would like be-

cause of experimental difficulties, there are definite indications of unusual substitution effects in the silanols (Table 2). For example, the  $\Delta H_{\text{acid}}^{\circ}$  values 354, 356, and 359 kcal/mol for  $\text{C}_6\text{H}_5\text{SiH}_2\text{OH}$ ,  $\text{C}_6\text{H}_5(\text{CH}_3)(\text{H})\text{SiOH}$ , and  $\text{C}_6\text{H}_5(\text{CH}_3)_2\text{SiOH}$  show that the  $\beta$ -replacement of a hydrogen by methyl decreases the silanol acidity 2-3 kcal/mol per substitution. In the methyl-substituted alcohol series, each methyl substitution increases acid strength by about 1-3 kcal/mol with  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{CH}_2\text{OH}$ ,  $(\text{CH}_3)_2\text{CHOH}$ , and  $(\text{CH}_3)_3\text{COH}$  having  $\Delta H_{\text{acid}}^{\circ}$  values of 380, 377, 375, and 374 kcal/mol. Similar indications of the importance of such inverse effects are evident for  $\beta$ -methyl substitution of  $\text{H}_3\text{SiOH}$  (a very small, but real effect), and perhaps  $(\text{CH}_3\text{O})_3\text{SiOH}$ , and  $\text{F}_3\text{SiOH}$  as well.

There are other aspects of the silanol acidities which are important. As we have seen for  $\text{C}_6\text{H}_5\text{SiH}_3$  versus  $\text{SiH}_4$  compared to toluene versus  $\text{CH}_4$ , an aromatic substitution, here an  $\alpha$  one, has only a small effect on the acidity of silicon compounds. In silanol comparisons of  $\beta$ -substitution effects, benzyl alcohol and  $\text{C}_6\text{H}_5\text{SiH}_2\text{OH}$  have acid strengths of 369 and 354 kcal/mol compared to 380 kcal/mol for methanol and

**Table 2.** The Acidity ( $\Delta H_{\text{acid}}^{\circ}$ ) of Substituted Silanols<sup>33</sup>

<i>Silanol</i>	$\Delta H_{\text{acid}}^{\circ}$ (kcal/mol)
$\text{SiH}_3\text{OH}$	358
$\text{CH}_3\text{SiH}_2\text{OH}$	359
$(\text{CH}_3)_2\text{SiHOH}$	359
$(\text{CH}_3)_3\text{SiOH}$	359
$\text{CH}_3\text{CH}_2(\text{CH}_3)_2\text{SiOH}$	359
$(\text{CH}_3\text{CH}_2)_2(\text{CH}_3)\text{SiOH}$	359
$(\text{CH}_3\text{CH}_2)_3\text{SiOH}$	359
$\text{C}_6\text{H}_5\text{SiH}_2\text{OH}$	354
$\text{C}_6\text{H}_5(\text{CH}_3)(\text{H})\text{SiOH}$	356
$\text{C}_6\text{H}_5(\text{CH}_3)_2\text{SiOH}$	359
$\text{CH}_3\text{O}(\text{CH}_3)_2\text{SiOH}$	359
$(\text{CH}_3\text{O})_2(\text{CH}_3)\text{SiOH}$	354
$(\text{CH}_3\text{O})_3\text{SiOH}$	354
$(\text{CH}_3\text{O})_2\text{SiHOH}$	354
$\text{F}(\text{CH}_3)_2\text{SiOH}$	354
$\text{F}_2(\text{CH}_3)\text{SiOH}$	346
$\text{F}_3\text{SiOH}$	339
$\text{Cl}_3\text{SiOH}$	323

358 kcal/mol for  $\text{SiH}_3\text{OH}$ . Since the phenyl substituent cannot interact conjugatively with either benzyl alcohol or  $\text{C}_6\text{H}_5\text{SiH}_2\text{OH}$ , its polarizability and inductive effects are the most critical features to explore. Both of these compounds should increase acidity with phenyl substitution since phenyl is characteristically a substituent with a large polarizability and a weak inductive electron withdrawing effect.<sup>46,47</sup> That the acid increasing effect of phenyl substitution is larger for the alcohols than the silanols is consistent with an explanation in which the polarizability effect of phenyl is attenuated in the silanol. Again, the distance dependence of the larger polarizability effect for phenyl is more critical with the silanol than the alcohol and, as a result, though the silanol is somewhat more acidic with phenyl substitution, the difference relative to the alcohols is attenuated.

A comparison of silanol acid strengths in which three substituents have replaced the three hydrogens of  $\text{SiH}_3\text{OH}$  (358 kcal/mol) can also be made. Both methyl and ethyl substitutions lead to only slight acid weakening [ $(\text{CH}_3)_3\text{SiOH}$  (359 kcal/mol) and  $(\text{CH}_3\text{CH}_2)_3\text{SiOH}$  (359 kcal/mol)]; however, polar substituents contribute to an increased acidity through their combined polarizability and inductive effects. Thus,  $(\text{CH}_3\text{O})_3\text{SiOH}$ ,  $\text{F}_3\text{SiOH}$ , and  $\text{Cl}_3\text{SiOH}$  have  $\Delta H_{\text{acid}}^\circ$  values of 354, 339, and 323 kcal/mol. It is perhaps surprising that three methoxy substitutions have so little effect on silanol acidity, but the methoxy substituent is known to exhibit both electron donating and withdrawing tendencies.<sup>46</sup> These counter-tendencies appear well balanced in  $(\text{CH}_3\text{O})_3\text{SiOH}$ . The extremely high acidity of  $\text{Cl}_3\text{SiOH}$  places it among the strongest gas phase acids, comparable in acidity to  $\text{HNO}_3$  and  $\text{HBr}$  (both 324 kcal/mol).<sup>22</sup> The greater acidity of  $\text{Cl}_3\text{SiOH}$  versus  $\text{F}_3\text{SiOH}$  is at first surprising, but such effects are not without precedent in the gas phase. The observation that  $\text{HCCl}_3$  is more acidic than  $\text{HCF}_3$  (352 and 375 kcal/mol)<sup>22</sup> can be attributed to polarizability effects in which the larger halogen of greater polarizability has a greater acidifying effect than the smaller, more electronegative fluorine. Despite the longer Si—Cl bond length (longer than Si—F by about 0.4 Å) in  $\text{Cl}_3\text{SiOH}$  versus  $\text{F}_3\text{SiOH}$ , the greater polarizability of chlorine overwhelms that of fluorine and is the critical factor controlling acidity, even over the distances in question.

The last six entries in Table 1 are from studies of anions of highly reactive silicon neutral compounds. Ion chemistry related to sila-acetone has been studied in some detail by three groups.<sup>34-36</sup> Sila-acetone is only slightly more acidic than acetone which is likely a

reflection of a greater stabilization of the carbanion in acetone than the corresponding one in silaacetone. Since an aromatic substitution has such a small  $\beta$ -effect on silanol acidity values, it is perhaps not surprising that the Si=O group does not effectively stabilize an adjacent carbanion as well as C=O does.

We have also measured the Si—H acidity of two Si=O containing compounds, namely H<sub>2</sub>SiO and CH<sub>3</sub>OSiHO.<sup>34,37</sup> An important aspect of these acidities must be considered at this point since each acidity is obtained by bracketing studies of its corresponding conjugate base. We have to consider whether those bases, [HSiO]<sup>-</sup> and [CH<sub>3</sub>OSiO]<sup>-</sup>, would be protonated at silicon as we suggest or at oxygen. This is a general problem faced in gas phase studies, namely that the structural identity of neutral products can only be inferred. Recognizing the limitations of our experimental approach, we have often turned to computational studies to guide our thinking. In the [HSiO]<sup>-</sup> case, we found that HSiOH and H<sub>2</sub>SiO had been studied computationally and their heats of formation were shown to be approximately equal.<sup>37</sup> Since these computations had not been carried out at the highest level available at the time of our work, we asked Professor Mark Gordon to consider this problem further. His results at the MP4/6-31G(d,p)//MP2/6-31G(d,p) level indicate that H<sub>2</sub>SiO is more stable than HSiOH by 2.7 kcal/mol.<sup>37</sup> Thus, we have indicated that the acidity which we measure is that of H<sub>2</sub>SiO. Because of its identical acidity and chemistry, CH<sub>3</sub>OSiHO is likely to be the acid corresponding to [CH<sub>3</sub>OSiO]<sup>-</sup>. Both of these silaaldehydes have acidities which are considerably greater than those of aldehydes [H<sub>2</sub>SiO is about 30 kcal/mol more acidic than formaldehyde or acetaldehyde].

In a related study, the acidity of the neutral SiCH<sub>2</sub> derives from bracketing studies<sup>38</sup> of [HCSi]<sup>-</sup>. Once again there is some ambiguity concerning such an anion. Indeed, would its conjugate acid be HSi≡CH or SiCH<sub>2</sub>? Extensive computations by several groups have established that SiCH<sub>2</sub> is far more stable than the silaacetylene.<sup>38</sup> Although the identity of the conjugate acid parent of [HCSi]<sup>-</sup> is certain, we have no suitable carbon analog for comparison. Nevertheless, we note that SiCH<sub>2</sub> is more acidic than acetylene by about 20 kcal/mol.

Finally, we have measured the acidities of dimethylsilene<sup>39</sup> and dimethylsilylene,<sup>40</sup> two organosilicon compounds of vital importance and considerable interest to silicon chemists. Acidities were measured by introducing these reactive neutrals, 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 are only approximate. Nevertheless, the C—H acidity of dimethylsilylene is about 15 kcal/mol greater than that of isobutene and dimethylsilylene is more acidic 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 polarizability and inductive effect differences between silicon and carbon. Dimethylsilylene, whose acid strength is approximately 379 kcal/mol, cannot be compared to its carbon analog since the latter has not been studied in the gas phase.

### 3.3. Other Thermochemical Properties of Silicon-Containing Compounds

Although far more limited in scope than acidity measurements, thermochemical determinations of a number of silicon-containing species have been carried out in the gas phase providing insight into the character of a number of unusual species.

The electron affinities (EA) (eq. 2b) of several silicon-centered radicals have been determined by electron photodetachment experiments of anions (Table 3) by Brauman and by Ellison and their respective co-workers.<sup>27,48</sup>

Since EA's are a measure of anion stabilities, EA values of 32.4 and 1.8 kcal/mol for the silyl and methyl radical show that  $\text{H}_3\text{Si}^-$  is far more stable toward electron detachment than  $\text{H}_3\text{C}^-$ . The data in Table

**Table 3.** Electron Affinities for Some Representative Silicon and Carbon Compounds

<i>Silicon-Containing Radical</i>	<i>EA (kcal/mol)</i>	<i>Carbon Analog</i>	<i>EA (kcal/mol)</i>
$\text{SiH}_3$	32.4 <sup>27,48</sup>	$\text{CH}_3$	1.8 <sup>22</sup>
$\text{SiD}_3$	32.0 <sup>48</sup>	$\text{CD}_3$	—
$\text{CH}_3\text{SiH}_2$	27.5 <sup>27</sup>	$\text{CH}_3\text{CH}_2$	-6.4 <sup>30</sup>
$(\text{CH}_3)_3\text{Si}$	22.4 <sup>27</sup>	$(\text{CH}_3)_3\text{C}$	-5.9 <sup>30</sup>
$\text{C}_6\text{H}_5\text{SiH}_2$	33.1 <sup>27</sup>	$\text{C}_6\text{H}_5\text{CH}_2$	19.9 <sup>30</sup>
$\text{C}_6\text{H}_5(\text{CH}_3)\text{SiH}$	30.7 <sup>27</sup>	$\text{C}_6\text{H}_5(\text{CH}_3)\text{CH}$	—
$(\text{CH}_3)_3\text{SiCH}_2$	21.9 <sup>28</sup>	$(\text{CH}_3)_3\text{CCH}_2$	4.8 <sup>30</sup>
$\text{Si}_2$	50.7 <sup>49</sup>	$\text{C}_2$	75.4 <sup>50</sup>

3 demonstrate that, unless carbanions have strongly stabilizing substituents like phenyl (large EA), they either have a weakly bound electron (small EA) or an unbound electron (negative EA).<sup>28,30,41</sup> Thus, benzyl anion is at least 20 kcal/mol more stable than the other carbanions tabulated.<sup>22</sup> In contrast, the silyl anions, even those having analogous substitution patterns to those of the carbanions, all have very strongly bound electrons.<sup>26,27</sup> The silabenzyl anion and  $\text{H}_3\text{Si}^-$  have nearly the same stability while methyl substitution leads to somewhat less stable silyl anions.<sup>26,27</sup> When viewed in the context of eq. 2, we see that the decrease in Si-H acidity on going from silane to methylsilane is a reflection of the EA's almost completely since the corresponding BDE's are almost identical.

Comparing the EA's of  $(\text{CH}_3)_3\text{SiCH}_2$  and  $(\text{CH}_3)_3\text{CCH}_2$  indicates that an  $\alpha$ -trimethylsilyl group has a tremendous stabilizing effect on a carbanion. In fact, this effect is about the same as that of a phenyl.<sup>22</sup> Thus, the large C—H acidity difference between methane and tetramethylsilane results from the EA differences not from radical stability changes (the BDE differences are small).<sup>26,27,42</sup>

Before the experimental determinations presented in Table 3 were published, we used measured  $\Delta\text{H}_{\text{acid}}^{\circ}$  values and published BDE's<sup>42</sup> to calculate (eq. 2) EA's for  $\text{H}_3\text{Si}$ ,  $\text{CH}_3\text{SiH}_2$ ,  $(\text{CH}_3)_2\text{SiH}$ ,  $(\text{CH}_3)_3\text{Si}$ ,  $\text{C}_6\text{H}_5\text{SiH}_2$ , and  $(\text{CH}_3)_3\text{SiCH}_2$ .<sup>26</sup> Agreement with the directly determined EA's of Brauman and co-workers<sup>27,28</sup> is good except for  $\text{CH}_3\text{SiH}_2$  and  $(\text{CH}_3)_3\text{SiCH}_2$  where there are 5–7 kcal/mol discrepancies between the directly measured and the calculated EA's. The discrepancies arise because our calculations have used slightly different acidities than those of Brauman and co-workers (see footnote to Table 1). Despite these differences, it is clear that the very large stabilities of silyl anions and  $\alpha$ -trimethylsilyl carbanions are easily recognized and that calculated EA's can provide useful information when direct measurements are unavailable, particularly if such calculations are prudently used.

The EA of  $\text{Si}_2$  has been determined by Ellison and co-workers to be 50.7 kcal/mol.<sup>49</sup> That of  $\text{C}_2$  is approximately 78 kcal/mol.<sup>50</sup> The electronic states of both  $\text{Si}_2$  and  $\text{Si}_2^-$  have been studied in detail; *ab initio* computational studies have been carried out to help interpret the complex photoelectron spectroscopy.<sup>49</sup>

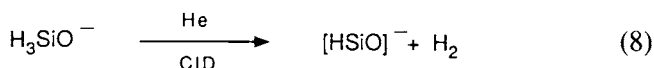
The EA measurements by Brauman and by Ellison and their respective co-workers have been used to calculate the Si-H BDE's of several silanes (Table 4).<sup>27,48</sup> That each of these derived BDE's is in good agreement with bond energy evaluations by other methods<sup>42</sup> provides an important internal calibration of quite different methods.



**Table 4.** Bond Dissociation Energies (BDE)  
Derived from Electron Affinities

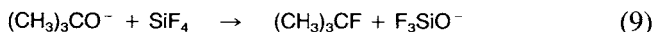
<i>Compound</i>	<i>BDE</i> ( <i>kcal/mol</i> )
H <sub>3</sub> Si-H	90.3 <sup>48</sup> (91.6) <sup>27</sup>
CH <sub>3</sub> SiH <sub>2</sub> -H	92.2 <sup>27</sup>
(CH <sub>3</sub> ) <sub>3</sub> Si-H	≥91.0 <sup>27</sup>
C <sub>6</sub> H <sub>5</sub> SiH <sub>2</sub> -H	90.2 <sup>27</sup>
C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )SiH-H	91.3 <sup>27</sup>

The heats of formation of several neutral compounds and negative ions have been obtained in gas phase negative ion experiments. For example, [HSiO]<sup>-</sup>, which is produced by collision-induced dissociation (CID) of H<sub>3</sub>SiO<sup>-</sup> (eq. 8), transfers H<sup>-</sup> to a number of reference



compounds allowing a determination of the hydride affinity (HA) of SiO of 49 kcal/mol<sup>37</sup> (see eqs. 4 and 5 for a review of these thermochemical quantities). Interestingly, HA<sub>SiO</sub> indicates that SiO binds hydride far more strongly than CO, its carbon analog, which has a HA of only 6 kcal/mol. From HA<sub>SiO</sub>, we have obtained the heat of formation of [HSiO]<sup>-</sup> (-38 kcal/mol from eq. 4b). This combined with ΔH<sub>acid</sub><sup>o</sup> for H<sub>2</sub>Si=O (eq. 5a) gave a heat of formation of -36 kcal/mol for H<sub>2</sub>Si=O. In a recent review, Walsh indicated that the best value of this heat of formation was -21.5 kcal/mol.<sup>42</sup>

McMahon and co-workers<sup>51</sup> have estimated the heats of formation of F<sub>2</sub>Si=O and F<sub>3</sub>SiO<sup>-</sup> from negative ion gas phase experiments on F<sub>3</sub>SiO<sup>-</sup>. This anion, prepared by eq. 9, transfers F<sup>-</sup> to various



reference neutrals allowing an estimation of the fluoride affinity (eq. 7a) of F<sub>2</sub>Si=O of 102 kcal/mol. Estimates of the heat of formation of F<sub>2</sub>Si=O (-231 kcal/mol) have been made based on thermochemical data for SiF<sub>4</sub> and SiO<sub>2</sub> and lead to a heat of formation for F<sub>3</sub>SiO<sup>-</sup> of -393 kcal/mol (eq. 10).<sup>51</sup> We have combined the heat of formation

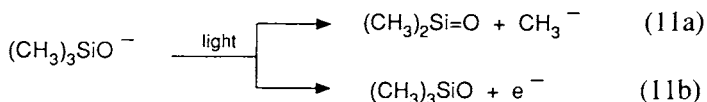
$$\Delta H_f^\circ(\text{F}_3\text{SiO}^-) = + \Delta H_f^\circ(\text{F}_2\text{SiO}) + \Delta H_f^\circ(\text{F}^-) - \text{Fluoride Affinity}(\text{F}_2\text{SiO}^-) \quad (10)$$

of  $F_3SiO^-$  with  $\Delta H_{acid}^{\circ}$  for  $F_3SiOH$  to obtain a heat of formation of  $F_3SiOH$  of  $-369$  kcal/mol.<sup>33</sup>

Since so few heats of formation of Si=O containing compounds and ions are known, it is difficult to assess the few thermochemical results that have been obtained from negative ion gas phase chemistry. Our 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)<sup>42</sup> are the only heats of formation for silanols of which we are aware. 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 with molecules determined by negative ion gas phase methods.

Negative ion gas phase chemistry has also provided information on the question of  $\pi$ -bond strengths of the silicon-to-carbon and silicon-to-oxygen double bonds. A recent study by Allison and McMahon reports on  $\pi$ -bond strengths for several substituted silenes.<sup>52</sup> Proton (positive ion chemistry) and fluoride (negative ion chemistry) affinity measurements have been used in two different thermochemical cycles, thus giving independent measures of the  $\pi$ -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  $\pi$ -bond strength. Estimates of the  $\pi$ -bond strengths of the analogous alkenes have been made using Benson type calculations and 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 128 kcal/mol. This latter value appears to us to be too small, given that fluoride ion reacts with allyltrimethylsilane to give allyl anion. Combining the EA's of both F and allyl and the BDE of allyltrimethylsilane gives a value for the Si-F BDE in  $(CH_3)_3SiF$  of about 143 kcal/mol.

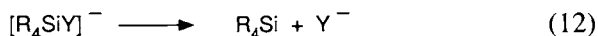
Brauman and co-workers have estimated a 62 kcal/mol upper limit on the  $\pi$ -bond strength in  $(CH_3)_2Si=O$  in a study of laser-induced fragmentation of  $(CH_3)_3SiO^-$  (eq. 11).<sup>36</sup> Analysis of the energetics of



these reaction channels as well as the those of the related fragmentation of  $(CH_3)_2(H)SiO^-$  allows the  $\pi$ -bond strength estimation based on the EA of  $CH_3$ , the BDE of a  $CH_3$ -Si bond, and estimates of two energy

terms. Comparisons of this experimental estimate and computational values obtained for simple silanones suggests that an upper limit of 62 kcal/mol is reasonable, particularly considering the difficulties faced in such experiments.

The general occurrence of pentacoordinate silicon anions (siliconates) has been established by negative ion gas phase chemistry.<sup>15-17,53-56</sup> Although siliconates have been accepted as gas phase species for some time, it is only recently that determinations of anion affinities of tetracoordinate silanes (see eq. 7a) have been made (Table 5)<sup>57-59</sup> and that the conditions under which siliconates form as intermediates in substitution reactions have been explored.<sup>60</sup> Anion affinity determinations provide a measure of the stability of siliconates (eq. 12) as do



recent computational studies.<sup>17</sup> Direct equilibrium measures of anion affinities for fluoride,<sup>57</sup> chloride,<sup>57</sup> and cyanide<sup>58</sup> have been carried out by McMahan and co-workers 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 is chloride. The fluoride effect results from the fluorine's small size, its greater covalent bond energies, and its greater basicity. Cyanide and chloride, which were found to make equally strong bonds to Bronsted acids in earlier studies by McMahan and co-workers,<sup>58</sup> have different bond strengths toward

**Table 5.** Anion Affinities of Tetracoordinate Silanes<sup>57,58,59</sup>

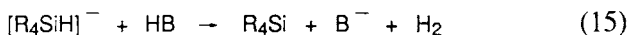
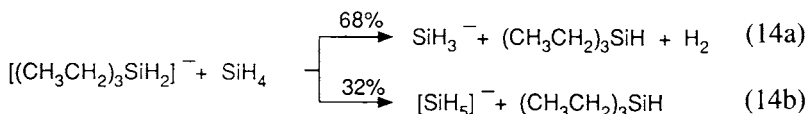
<i>Compound</i>	<i>Anion</i>	<i>Anion Affinity (kcal/mol)</i>
(CH <sub>3</sub> ) <sub>4</sub> Si	F	29.9
(CH <sub>3</sub> ) <sub>3</sub> SiF	F	38.2
(CH <sub>3</sub> ) <sub>2</sub> SiF <sub>2</sub>	CN	16.8
CH <sub>3</sub> SiF <sub>3</sub>	F	50.5
CH <sub>3</sub> SiF <sub>3</sub>	Cl	16.1
CH <sub>3</sub> SiF <sub>3</sub>	CN	22.6
SiF <sub>4</sub>	F	62
SiF <sub>4</sub>	Cl	23.4
SiF <sub>4</sub>	CN	27.2
SiCl <sub>4</sub>	Cl	24.2
SiH <sub>4</sub>	H	~ 22
n-C <sub>5</sub> H <sub>11</sub> SiH <sub>3</sub>	H	~ 11
(CH <sub>3</sub> CH <sub>2</sub> ) <sub>3</sub> SiH	H	~ 10

silicon where more covalent bonding occurs. In addition, the anion affinities parallel the substituent effects seen in gas phase acidities. Thus, for the series  $\text{CH}_3\text{SiF}_3$ ,  $(\text{CH}_3)_2\text{SiF}_2$ ,  $(\text{CH}_3)_3\text{SiF}$ , and  $(\text{CH}_3)_4\text{Si}$ , the anion affinities decrease as do the C—H acidities. Such trends are also observed for other main group elements.

Hajdasz and Squires have used the thermochemical cycle generalized in equation 7 to obtain the hydride affinities of several simple silanes (Table 5).<sup>59</sup> They discovered that hydridosiliconates could be prepared by direct reaction (eq. 13). Thus,  $(\text{CH}_3)_4\text{Si}$ ,  $(\text{CH}_3\text{CH}_2)_3\text{SiH}$ ,



$(\text{CH}_3\text{CH}_2)_2\text{SiH}_2$ , and  $n\text{-C}_5\text{H}_{11}\text{SiH}_3$  could be efficiently converted to their hydridosiliconates. The hydridosiliconates undergo hydride transfer reactions with silanes (eq. 14) and other acids (eq. 15). Using a



series of acids in studying reactions like those in equation 15, the hydride affinities of  $\text{SiH}_4$ ,  $n\text{-C}_5\text{H}_{11}\text{SiH}_3$ , and  $(\text{CH}_3\text{CH}_2)_3\text{SiH}$  were shown to be approximately 22, 11, and 10 kcal/mol. These hydride affinities are among the lowest known for neutral molecules (recall that HA for CO is 6 kcal/mol). Such low hydride affinities are expected from computational studies, especially on  $\text{SiH}_4$ , which predict values around 20 kcal/mol.<sup>17,59</sup>

We have carried out a closely related study on siliconates in which flowing afterglow experimental studies were combined with extensive computational work.<sup>17</sup> Anion affinities with varying substituents and varying anions (eq. 16) were predicted by both AM1 and *ab initio*



methods (in collaboration with L. W. Burggraf, L. P. Davis and M. S. Gordon). In most instances, the semiempirical MNDO methods gave a reasonable indication of the energetics of reaction, but the *ab initio* results acted as the standard for these studies. The FA experiments were designed to test the generality of the computations and, as a

result, some 20 new siliconates were prepared which had hitherto been unknown and which were predicted to be stable by the computational studies. Although 91 combinations of X and Y were studied, only five of these (X = SiH<sub>3</sub> and Y = CH<sub>3</sub>, NH<sub>2</sub>, OCH<sub>3</sub>, F, or H) were predicted to be unstable (i.e., to have negative anion affinities). All other combinations of X = Y = OH, OCH<sub>3</sub>, CH<sub>3</sub>, NH<sub>2</sub>, H, PH<sub>2</sub>, SH, SCH<sub>3</sub>, F, Cl, Br, I, and SiH<sub>3</sub> had positive anion affinities. Interestingly, the observations of Larson and McMahon<sup>57</sup> and Hajdasz and Squires<sup>59</sup> are readily accommodated by the 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<sub>3</sub>, 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<sub>3</sub> and H are reasonably consistent with experiment. The extremely large hydride affinities for Y = SH and Cl are remarkable and reminiscent of other differing effects for second and third row elements.<sup>61</sup> It might appear that the thermochemical cycle given in equation 7 would be suitable for studying the large hydride affinity of SH and Cl, but these computations show that direct hydride reactions would lead to loss of HS<sup>-</sup> and Cl<sup>-</sup> through a very low energy exit channel.

## 4. REACTIVITY STUDIES ON SILICON COMPOUNDS

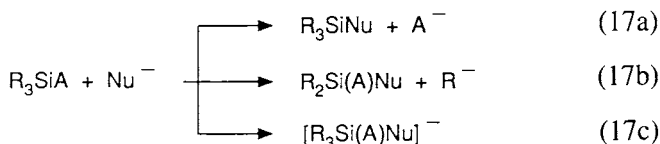
### 4.1. General Comments on Reactivity Studies

The sections which follow deal with several aspects of the negative ion chemistry of silicon compounds. Three broad classifications will serve to organize these sections. In Section 4.2, we will consider reactions which lead to the formation of stable unstable carbanions. In so doing, we will examine what different results are obtained as the negative ion and the structure of the silicon compounds varies. In Section 4.3, reactions in which stable siliconates are formed as well as reactions leading to other silicon-containing anions are considered as are studies of their reactivity. Still other silicon-containing anions which have been prepared using tandem FA-SIFT and collision-induced dissociation (CID) techniques are discussed in Section 4.4. In considering the details of these reactivity studies, we have tried to emphasize the general reactivity features of silicon-containing anions

and neutrals. These studies have thus begun to define an area of silicon chemistry hitherto unknown.

#### 4.2. Reactions Between Negative Ions and Silanes: Formation of Carbanions

Gas phase reactions between anions ( $\text{Nu}^-$ ) and silanes can take different paths depending on the nature of the anion and/or the structure of the silane (eq. 17). Such reactions have been reviewed recently.<sup>41</sup>

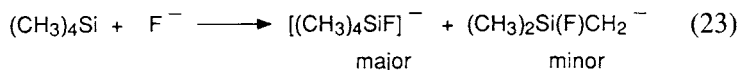


The treatment given here will consider aspects not previously reviewed for silicon chemists as well as some recent developments. In 1980 DePuy and co-workers reported that stable carbanions could be prepared in the gas phase by reaction 17a for several different A groups.<sup>62</sup> Although that study focused primarily on preparing regiospecific carbanions using fluoride ion as the nucleophile, it gave the first indications of the complexity of reaction 17. (Related work at about this time by Bowie and co-workers explored the nature of such reactions with alkoxides).<sup>63</sup> Thus, while fluoride gives the desired regiospecific carbanions if  $\text{A}^-$  is a good leaving group, cleavage reactions (eq. 17b) and/or siliconate formation (17c) occur when  $\text{A}^-$  is a poorer leaving group. Equations 18 and 19 are examples of successful regiospecific forma-

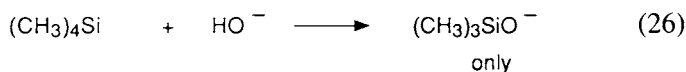
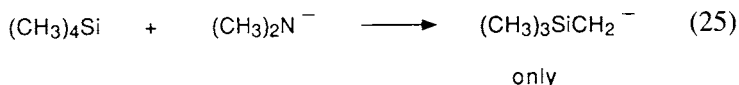
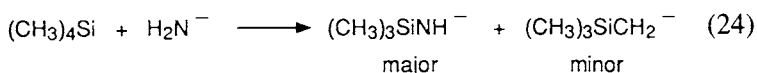


tion of isomeric carbanions; these reactions give about 90% of the carbanion along with a small amount of proton abstraction product (M-1) not included in equation 17. Similar results were reported for the allyl and benzyl carbanions<sup>62</sup> and more recently with the acetyl anion.<sup>64</sup> This method of carbanion generation continues to be of importance as indicated by the preparation and study of the thiomethyl anion<sup>65</sup> and other carbanions.<sup>28,66,67</sup> One very interesting observation along these lines has recently been made by Chou and Kass<sup>68</sup> who have demonstrated that regio- and stereoisomers of vinyl anions can be made at





somewhat different way (eq. 24)<sup>62</sup> as does tetramethylsilane with dimethylamide (eq. 25)<sup>69</sup> and with hydroxide (eq. 26).<sup>29,30,41,62</sup> These



results with tetramethylsilane cannot be explained simply, although intermediate formation of a silicate is probable in equations 23, 24, and 26. While cleavage reactions occur for fluoride, amide, and hydroxide, they do so to different extents. Not only can  $\text{Nu}^-$  react directly as a base to give an M-1 product (eqs. 24 and 25), but silicates can form with excess energy (analogous to **1** in eq. 22) and  $\text{CH}_3^-$  can be lost giving complexes like **2** in equation 22. For fluoride, which is the weakest base among these anions, adduct formation predominates with only a small amount of cleavage occurring. Here the cleavage product results from  $\text{CH}_3^-$  abstraction of a C-H whose acidity value is about 387 kcal/mol ( $\Delta\text{H}_{\text{acid}}^\circ$  for  $\text{CH}_4$  is 417 kcal/mol, so such a proton abstraction would be 30 kcal/mol exothermic). With amide, only a small amount of M-1 results even though this is a very exothermic channel; the major process is cleavage from an N-H in  $(\text{CH}_3)_3\text{SiNH}_2$  whose acidity is about 379 kcal/mol (38 kcal/mol exothermic). When dimethylamide reacts, only M-1 occurs since a cleavage analogous to that with amide cannot take place because dimethylamide has no N-H. It is surprising that no  $\text{CH}_3^-$  forms since a C-H abstraction would be quite exothermic. Hydroxide, which is a weaker base than amide or dimethylamide and a stronger one than fluoride, has about the same basicity as  $(\text{CH}_3)_4\text{Si}$ . Thus, we would expect methyl cleavage to predominate for much the same reasons it does with amide, but, because of hydroxide's weaker basicity, we would not expect much M-1, which is consistent with the result that no such products are observed.

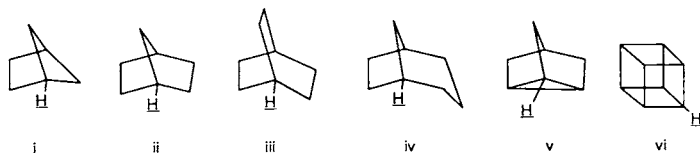




**Table 6.** Acidities Derived from the Silane Cleavage Branching Ratios<sup>30</sup>

<i>R</i>	<i>Experimental</i> $\Delta H_{acid}^{\circ} (RH)^{a,b}$
Ethyl	420.1
Isopropyl	419.4
Cyclobutyl	417.4
Methyl	(416.6)
Cyclopentyl	416.1
<i>sec</i> -Butyl	415.7
<i>n</i> -Propyl	415.6
<i>tert</i> -Butyl	413.1
Isobutyl	412.9
3-Butenyl	412.0
Cyclopropyl	411.5
Cyclopropylmethyl	410.5
1-Methylcyclopropyl	409.2
Neopentyl	408.9
Vinyl	407.5
2-Propenyl	405.8
Phenyl	(400.7)
i <sup>c</sup>	417
ii <sup>c</sup>	414
iii <sup>c</sup>	414
iv <sup>c</sup>	414
v <sup>c</sup>	408
vi <sup>c</sup>	412

<sup>a</sup> Parentheses denote reference values. <sup>b</sup> The errors in the relative acidities are  $\pm 1 \text{ kcal mol}^{-1}$ . <sup>c</sup> The structures of i-vi are given below.

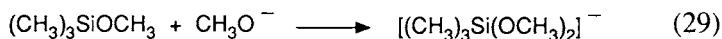


tion is beyond the scope of this article. This brief description serves to emphasize for silicon chemists the role that silicon compounds have played in this story.<sup>71</sup>

### 4.3. Reactions Between Negative Ions and Silanes: Formation of Silicon-Containing Anions

Although some of the details of the intermediacy of siliconates in carbanion formation have been considered, a more operational ap-

proach will serve in this brief discussion of siliconate formation and reactivity. Siliconates as major products in ion-molecule reactions were reported as early as 1970;<sup>53-55</sup> however, work commencing around 1980 established that siliconates are frequently encountered in the negative ion gas phase chemistry of silicon and that they have interesting properties.<sup>15,16,56</sup> In general terms, siliconates efficiently form in reactions between nucleophiles and silanes lacking a good leaving group. Two additional requirements are: (1) that the nucleophile lack an easily abstracted hydrogen; and (2) that the nucleophile not be too strong a base, thus minimizing cleavage and proton abstraction channels. A number of examples of siliconate formation under such conditions have been reported (eqs. 13, 23, and 29). We have also shown



that it is possible to prepare siliconates when the general conditions just mentioned are not met. Recognizing from our computational studies that virtually every siliconate can be formed exothermically, we demonstrated that the appropriate choice of reactants could determine the success of siliconate formation.<sup>17</sup> Thus, the siliconate  $[(\text{CH}_3)_3\text{Si}(\text{F})(\text{H})]^-$  could be formed either from  $(\text{CH}_3)_3\text{SiF}$  and hydride or from  $(\text{CH}_3)_3\text{SiH}$  and fluoride. Our computations, although based on the unsubstituted case for computational simplicity, indicated that only the substitution reaction leading to  $(\text{CH}_3)_3\text{SiH}$  and fluoride should occur in the  $(\text{CH}_3)_3\text{SiF}$  plus hydride direction (since the exothermicity  $[(\text{CH}_3)_3\text{Si}(\text{F})(\text{H})]^-$  formation channel, 42 kcal/mol in this case, would allow escape through the substitution products channel) (see Figure 3).<sup>17</sup> On the other hand,  $(\text{CH}_3)_3\text{SiH}$  and fluoride should react allowing

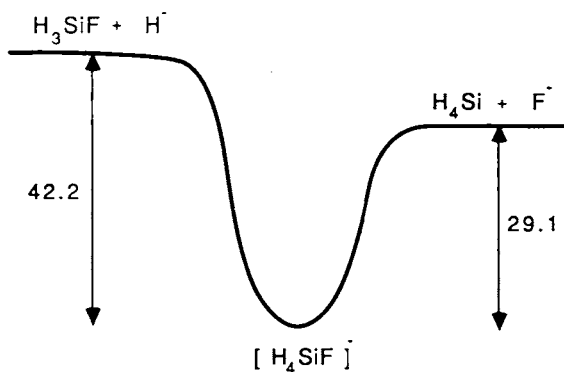
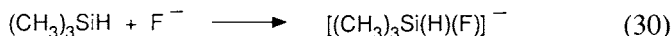
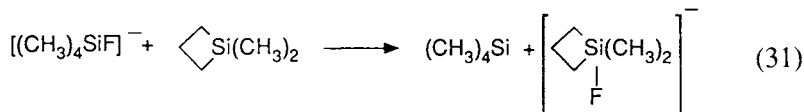


Figure 3

the siliconate to be stabilized by collisions with the buffer gas (29 kcal/mol) since the the substitution exit channel in this direction would be endothermic. Indeed, we have been able to demonstrate the validity of such an analysis for this as well as other examples (eq. 30):



Another important aspect of siliconate gas phase chemistry is represented in equation 31. It shows that fluoride can be "soft" transferred



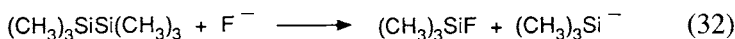
from  $[(\text{CH}_3)_4\text{SiF}]^-$  to dimethylsilacyclobutane (DMSCB).<sup>16</sup> In view of the angle strain of DMSCB, it might be expected that ring opening would dominate any of its reactions. Indeed, direct reaction of DMSCB and fluoride gives the siliconate in only 40% yield along with 60% of a ring cleavage product. On the other hand, a number of such soft anion transfers have carried out; among the most interesting are those reported by Hajdasz and Squires in their studies of  $[\text{SiH}_5]^-$  (eq. 14b).<sup>59</sup>

Soft anion transfers are easily understood from the computational studies in which a typical direct reaction to form a siliconate is highly exothermic, but a related transfer reaction is less exothermic.<sup>17</sup> For example, experimental attempts to prepare  $[(\text{CH}_3)_3\text{Si}(\text{Cl})\text{N}(\text{CH}_3)_2]^-$  by direct reaction between dimethylaminotrimethylsilane and chloride failed while transfer from  $[(\text{CH}_3)_4\text{SiCl}]^-$  gave the desired siliconate. Our computational work on the unsubstituted systems suggests that the direct reaction is about 9 kcal/mol exothermic while the transfer reaction is only about 1 kcal/mol exothermic. Although this particular analysis depends on AM1 computations which are always subject to critical discussion, related *ab initio* results give similar results. Thus, it is clear that many direct reactions to form siliconates, while favorable energetically, give siliconates too energetic to be stabilized under gas phase conditions. Transfer of an anion to form a siliconate is often more successful than direct reaction because the resulting siliconate is formed in a less exothermic reaction.

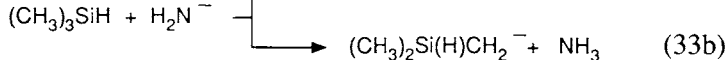
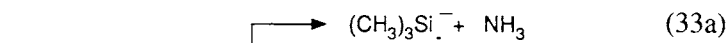
We have used soft transfer reactions to determine some crude fluoride affinities by bracketing techniques<sup>16</sup> although more recent methods<sup>57-59</sup> (including computations)<sup>17</sup> are now preferred (Section 3.1.

eq. 7a, and Section 3.3, eqs. 13, 14, and 16). We have found that three different silacyclobutanes (each tetraalkyl substituted) have fluoride affinities that are 15–20 kcal/mol greater than those of dimethylsilacyclohexane or other tetraalkylsilanes. This striking difference is attributed to geometrical factors which give unusual stability to the siliconates of the silacyclobutanes. Thus, strain is relieved for the silacyclobutanes as they approach the trigonal bipyramidal geometry of the siliconates.

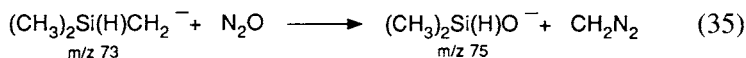
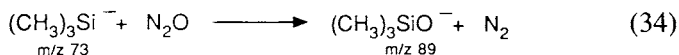
Examples of reactions in which silicon-containing anions are formed have been given in earlier sections. We have seen that hydroxide cleavage of silanes gives siloxide ions (eqs. 26 and 28) which have played critical roles in studies of the acidities of silanols (Table 2) and weakly acidic hydrocarbons (Table 6). Similarly, proton abstraction reactions can lead to  $\alpha$ -silyl carbanions (eqs. 24–25) and reactions with  $F^-$  can lead to both carbanions (eqs. 18–20) and silyl anions (eq. 32).<sup>26,72</sup>



A practical question which has yet to be addressed is how do we know the structure of these various product anions, especially since we detect only a mass-to-charge ( $m/z$ ) ratio in our negative ion gas phase experiments? Some of these structures are based on assumptions about the mechanisms of the reactions studied. Oftentimes, however, more information is required. As a result, we have sought to find specific chemical reactions for different anion types to be used for qualitative structure determination.<sup>72,73</sup> The proton abstraction reaction of methylsilane (eq. 33) serves as an excellent example since measurement of



the  $m/z$  73 product anion is consistent with both the silyl anion (eq. 33a) and the  $\alpha$ -silyl carbanion (33b) formulation. We have found in independent experiments that silyl anions and  $\alpha$ -silyl carbanions react differently with  $\text{N}_2\text{O}$  (eqs. 34–35);<sup>72</sup> therefore, the appearance of sig-



nals at both  $m/z$  75 and 89 demonstrate that both isomeric anions are produced in equation 33. This suggests that the reaction is kinetically, not thermodynamically controlled.<sup>26</sup> Also using  $N_2O$  as a diagnostic, we have shown that only  $(CH_3)_2Si(CH=CH_2)CH_2^-$  is present as the M-1 product in the reaction of amide and vinyltrimethylsilane.<sup>72</sup>

Other reagents have also been used to characterize silicon-containing anions. Typically,  $N_2O$ ,  $CO_2$ ,  $CS_2$ , and  $COS$  distinguish and characterize silyl anions,  $\alpha$ -silyl carbanions, and siloxides.<sup>26,34,37,38,72</sup> Table 7 summarizes these reactions. Still other characterizing reagents like  $SO_2$ ,  $CH_3NCO$ , and  $CH_3NCS$  have also been used, but to a lesser extent.<sup>37,74,75</sup> In collaborative work with Sheldon, Bowie, and co-workers, we have combined both experimental and computational work to understand the reaction mechanisms of some of these characterizing reagents with silyl anions<sup>74</sup> and siloxides.<sup>75</sup> Rate coefficient measurements of  $H_3Si^-$  and  $(CH_3)_3Si^-$  reacting with  $CO_2$ ,  $COS$ ,  $CS_2$ ,  $SO_2$ ,  $N_2O$ ,  $CH_3NCO$ , and  $CH_3NCS$  have been carried out and the efficiencies of these reactions have been estimated. Computational studies, carried out at the 6-31G *ab initio* level for  $H_3Si^-$  reacting with  $CO_2$ ,  $CS_2$ ,  $SO_2$ , and  $N_2O$ , reveal the broad outlines of the reaction dynamics. Thus, the  $CO_2$  reaction has been shown to involve silicon

**Table 7.** Summary of the Reactions Used to Characterize Silicon-Containing Anions<sup>15,72,74,75</sup>

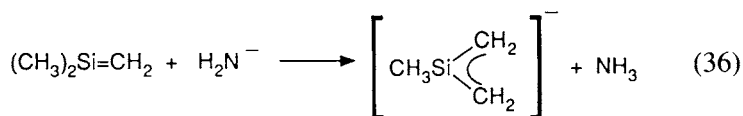
Silicon-Containing Anion	Characterizing Reagent	Anionic Product
$(CH_3)_3Si^-$ <sup>a</sup>	$N_2O$	$(CH_3)_3SiO^-$
$(CH_3)_3SiCH_2^-$	$N_2O$	$(CH_3)_3SiO^-$
$(CH_3)_3SiO^-$	$N_2O$	NR
$(CH_3)_3Si^-$	$CO_2$	$(CH_3)_3SiO^-$
$(CH_3)_3SiCH_2^-$	$CO_2$	$(CH_3)_3SiO^-$
$(CH_3)_3SiO^-$	$CO_2$	$(CH_3)_3SiOCO_2^-$
$(CH_3)_3Si^-$ <sup>b</sup>	$CS_2$	$(CH_3)_3SiS^-$
$(CH_3)_3SiCH_2^-$	$CS_2$	$(CH_3)_3SiS^-$
$(CH_3)_3SiO^-$	$CS_2$	$(CH_3)_3SiS^-$
$(CH_3)_3Si^-$	$COS$	$(CH_3)_3SiS^-$
$(CH_3)_3SiCH_2^-$	$COS$	$(CH_3)_3SiS^-$
$(CH_3)_3SiO^-$	$COS$	$(CH_3)_3SiS^-$

<sup>a</sup> Recent experiments show that  $(CH_3)_2SiHSi(CH_3)_2^-$  does not react with  $N_2O$ .<sup>32</sup>

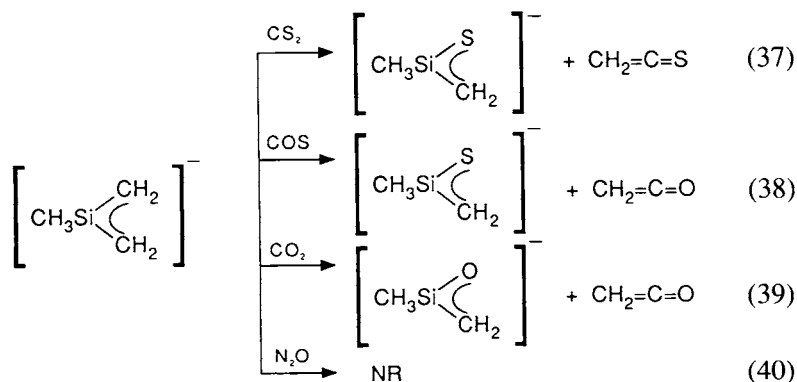
<sup>b</sup> Recent experiments show that  $(CH_3)_2SiHSi(CH_3)_2^-$  reacts with  $CS_2$  to give  $(CH_3)_2SiHSi(CH_3)_2S^-$ .

attack at carbon while the  $\text{CS}_2$  reaction, which has a very different type of product, likely occurs by attack at sulfur. Even though there is a strongly exothermic reaction pathway for carbon attack in the  $\text{CS}_2$  reaction, it is possible that the adduct,  $\text{H}_3\text{SiCS}_2^-$ , cannot be stabilized by collision since its formation is more exothermic than formation of  $\text{H}_3\text{SiCO}_2^-$ . Both the reaction with  $\text{SO}_2$  and  $\text{N}_2\text{O}$ , which experimentally yield  $\text{H}_3\text{SiO}^-$ , are computationally complex. A related study reports kinetic and computational aspects of  $\text{H}_3\text{SiO}^-$  and  $(\text{CH}_3)_3\text{SiO}^-$  reacting with  $\text{CS}_2$ ,  $\text{COS}$ , and  $\text{CH}_3\text{NCS}$ , each giving  $\text{R}_3\text{SiS}^-$ . The computational studies carried out at the 6-31G and 6-31++G levels for  $\text{CS}_2$  plus  $\text{H}_3\text{SiO}^-$  suggest that attack at carbon leads by a highly exothermic path to  $\text{H}_3\text{SiOCS}_2^-$ . 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 is the likely transition state leading to  $\text{H}_3\text{SiS}^-$  and  $\text{COS}$ .

Characterizing reagents and computations have played a prominent role in our studies of dimethylsilene<sup>39</sup> and dimethylsilylene,<sup>40</sup> both of which have been generated in the FA by pyrolysis of standard precursors (Section 3.2). When dimethylsilene, which has been generated from dimethylsilacyclobutane, reacts with either hydroxide or amide, its M-1 anion is generated (eq. 36). Its reactions with  $\text{CS}_2$ ,  $\text{COS}$ ,  $\text{CO}_2$ ,

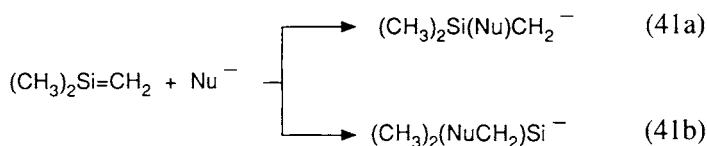


and  $\text{N}_2\text{O}$  (eqs. 37–40) support the silaallyl anion formulation. Reaction



with CS<sub>2</sub>, COS, and CO<sub>2</sub> are typical of α-silyl carbanions with CH<sub>2</sub> being replaced as shown. Since N<sub>2</sub>O is the least reactive of these characterizing reagents,<sup>39</sup> it is perhaps not surprising that there is no reaction with the silyallyl anion, which itself would be expected to have attenuated reactivity because of its lower basicity (see Table 1).

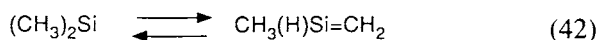
We have also investigated the addition of Nu<sup>-</sup> to dimethylsilene.<sup>40</sup> Our kinetically controlled proton abstraction studies<sup>26</sup> as well as computational work in collaboration with Professor M. S. Gordon clearly indicate that silyl anions are usually more stable than their corresponding α-silyl carbanions.<sup>76</sup> Thus, for Nu<sup>-</sup> addition to dimethylsilene, we would expect that addition should be favored at carbon (eq. 41b) if no



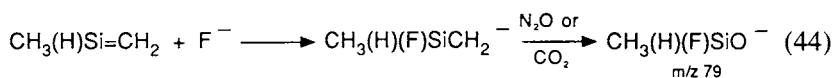
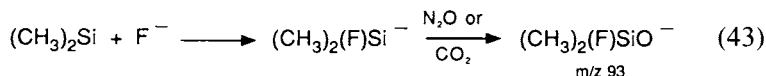
other strongly perturbing effects are operating. Despite this, characterizing reagents have established that both allyl anion and cyanide add to dimethylsilene by reaction at the silicon center (eq. 41a).<sup>39</sup> Thus, kinetic rather than thermodynamic factors control the reactivity.

Dimethylsilylene generated from 1,2-dimethoxy-1,1,2,2-tetra-methyl-disilane reacts with amide to give CH<sub>3</sub>SiCH<sub>2</sub><sup>-</sup>, an anion which is remarkably unreactive.<sup>40</sup> Although it reacts with CS<sub>2</sub> to give CH<sub>3</sub>SiS<sup>-</sup>, it fails to react with COS or CO<sub>2</sub>. Computational studies of this anion by Gordon<sup>40</sup> indicate that a significant amount of the negative charge is on silicon, suggesting that its attenuated reactivity results because it is not a typical α-silyl carbanion.

We have used N<sub>2</sub>O and CO<sub>2</sub> to show that the silylene-silene isomerization (eq. 42)<sup>40</sup> can be explored in the flowing afterglow. Dimethyl-



silylene dominates this equilibrium at low temperatures; thus, we explored the reaction with fluoride as the pyrolysis temperature increased. Equations 43 and 44 describe the relevant chemistry. At low

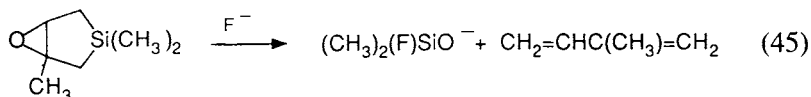




temperatures,  $m/z$  93 dominates; as the temperature increases, so does  $m/z$  79. Although a number of other products are expected to “funnel off” from this isomerization, the rates at which such reactions occur are slow relative to equation 42.<sup>40</sup> As a result, we have been able to use flowing afterglow techniques to study the isomerization without such added complications.

Squires and co-workers have reported interesting observations on the reaction of silaacetone enolate and various alcohols.<sup>35</sup> Since no H/D exchange occurred with  $\text{CH}_3\text{OD}$ ,  $\text{CH}_3\text{CH}_2\text{OD}$ , or  $(\text{CH}_3)_2\text{CHOD}$ , in contrast to the behavior of acetone enolate, a comprehensive examination of the ionic products of other alcohols was undertaken. It revealed that two main processes were occurring. In each pathway, the silaacetone enolate and alcohol form a complex in which proton transfer occurs. In the resulting alkoxide-silaacetone complex, alkoxide adds to  $\text{Si}=\text{O}$  giving a tetracoordinate silicon anion,  $(\text{CH}_3)_2(\text{RO})\text{SiO}^-$ . If R can undergo six-centered elimination, then alkene is lost and  $(\text{CH}_3)_2(\text{HO})\text{SiO}^-$  results (for example,  $\text{R} = \text{CH}_3\text{CH}_2$ ,  $(\text{CH}_3)_2\text{CH}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$ , and  $(\text{CH}_3)_3\text{C}$ ). If, however, R cannot undergo elimination, then methane is lost and the silaester enolate,  $\text{ROSi}(=\text{O})\text{CH}_2^-$  results ( $\text{R} = \text{C}_6\text{H}_5\text{CH}_2$  and  $(\text{CH}_3)_3\text{CCH}_2$ ).

A final example of a reaction resulting in a silicon-containing anionic product is shown in equation 45.<sup>77</sup> This complex reaction is



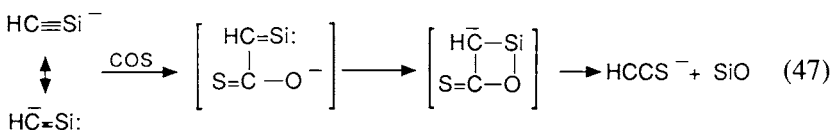
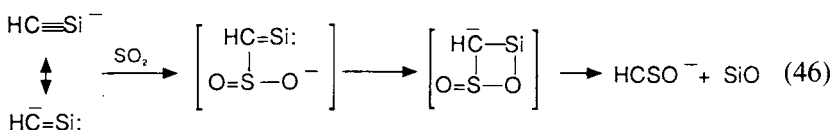
probably initiated by fluoride attack at silicon, but the details of how the siliconate so formed decomposes are difficult to assess. We have indicated that either a concerted decomposition or stepwise ones with silaoxetane intermediates are possible. Other examples of such isoprene extrusions have been examined for both spiro compounds related to the reactant in equation 45 and for a related germanium analog.<sup>77</sup>

#### 4.4. Silicon-Containing Anions from Selected Ion Flow Tube (FA-SIFT) and Collision-Induced Dissociation (CID) Studies

As previously discussed, the introduction of tandem flowing afterglow techniques (see Figure 2) has added important dimensions to studies of silicon-containing anions. Both the potential of selecting an individual ion from a complex reaction mixture and that of cleanly

producing new ions from collision-induced dissociation has been realized.

We first applied these techniques in a study looking for evidence of the long sought-after silicon-carbon triple bond.<sup>38</sup> Electron impact of methylsilane in the tandem FA-SIFT source led to a very complex array of some twenty anions from which the anion with  $m/z$  41 was mass selected.<sup>38</sup> This anion corresponds to one containing a hydrogen, silicon, and carbon atom. Since anions are formed in the high energy plasma of the source before they are stabilized by collision, their molecular structure cannot be inferred from the starting material. Both chemical studies using characterizing reagents (eqs. 46–47)<sup>38</sup> and com-

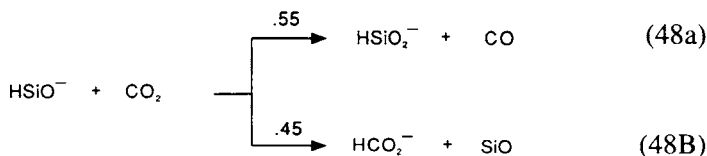


putational studies by Schmidt and Gordon<sup>78</sup> indicate that the  $m/z$  41 anion should be formulated as  $[\text{HCSi}]^-$ . Reaction with both  $\text{SO}_2$  and  $\text{COS}$  are best understood if the carbon in  $[\text{HCSi}]^-$  acts as the nucleophilic center attacking sulfur and carbon, respectively. Whether nucleophilic attack and ring formation is sequential (as shown) or concerted is unknown; however, a  $[\text{CSiH}]^-$  formulation for  $m/z$  41 is inconsistent with these reactions. Carbon dioxide reacts with  $m/z$  41 in a manner analogous to reaction 47, but this result can only be discerned by  $\text{CO}_2$  labeling experiments since the unlabelled ketene anion product,  $\text{HCCO}^-$ , has the same  $m/z$  as  $[\text{HCSi}]^-$ . Reaction with  $\text{CS}_2$  does not occur. Schmidt and Gordon in their detailed computational study of these reactions offer two important insights that could not be deduced from the experimental work. First, they suggest that reaction 47 has a channel giving  $\text{HCCO}^-$  and  $\text{SiS}$  that we have not probed experimentally. Since this channel gives an anionic product with  $m/z$  41, we could probe it only with oxygen-labelled  $\text{COS}$ , but its high cost has deterred us. They also indicate that, while the product energies for reaction with  $\text{CS}_2$  are thermochemically favorable, the

initial interaction between  $[\text{HCSi}]^-$  and  $\text{CS}_2$  must overcome a 20 kcal/mol barrier [MP2/6-31 + G(d)]. Since in the reactions of  $\text{SO}_2$ ,  $\text{CO}_2$ , and  $\text{COS}$  no such barrier is present, it is not surprising that they react and  $\text{CS}_2$  does not. The computational study verifies our suggestion based on the experimental work that such reactions pass through a stable, cyclic intermediate anion; in fact, considerable detail concerning the respective reaction pathways has been provided by Schmidt and Gordon (see Chapter in this volume by Mark S. Gordon).

The location of hydrogen on carbon in  $[\text{HCSi}]^-$  begs the question of bonding between carbon and silicon. Indeed, is this a triply bonded anionic species? A simple mechanistic analysis (eqs. 46–47) certainly suggests that triple bond character may be important, but clearly negative charge on carbon is required as well.<sup>38</sup> Computations by Schmidt and Gordon unequivocally indicate that the anion is best thought of as a silicon-carbon triple bonded species.<sup>78</sup> Despite this, the proper formulation of the conjugate acid of  $[\text{HCSi}]^-$  is  $\text{H}_2\text{C}=\text{Si}$ : as we have previously indicated (Section 3.2).

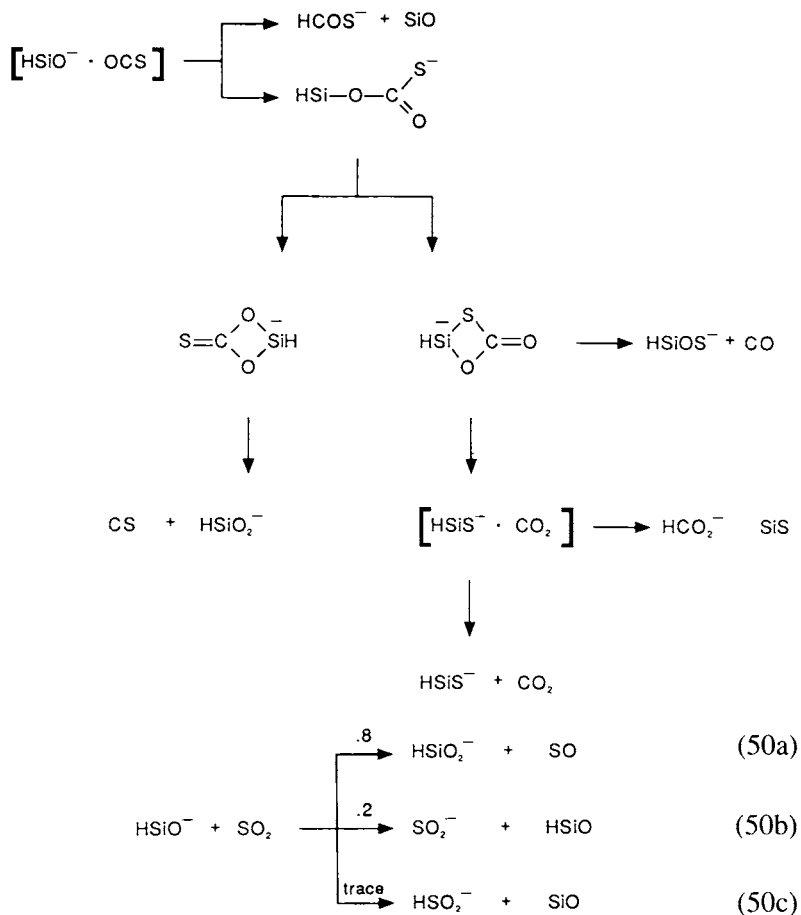
In two recent studies we have examined the formation of  $[\text{RSiO}]^-$  species by CID and their chemistry.<sup>34,37</sup> These studies sought to probe the relationship of such anions to their neutral  $\text{Si}=\text{O}$  parent compounds. The thermochemical aspects of this work have already been considered (Sections 3.2 and 3.3). When  $\text{R} = \text{H}$  (eq. 8),  $[\text{HSiO}]^-$  can be cleanly studied in the tandem FA-SIFT.<sup>37</sup> Its reaction chemistry has been extensively studied; several of its more interesting reactions are given in equations 48–51.<sup>37</sup> Because several of these reactions have products with identical  $m/z$ 's, extensive use of labeling was required to fully elucidate the products. For example, in the  $\text{CO}_2$  reaction (eq. 48),



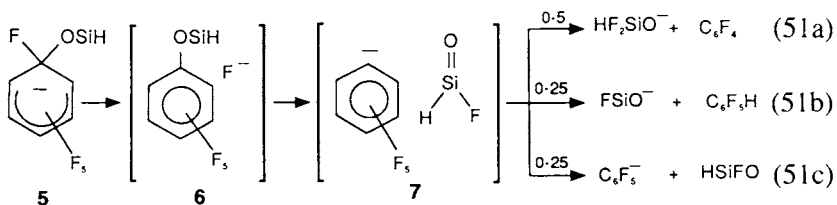
we found that only about 50% of the  $[\text{HSiO}]^-$  signal was converted to  $\text{HSiO}_2^-$  even at high  $\text{CO}_2$  flows. Reaction with labeled  $\text{CO}_2$  revealed another anionic product, namely  $\text{HCO}_2^-$ . While hydride transfer to  $\text{CO}_2$  is a common gas phase reaction, oxygen atom transfer by  $\text{CO}_2$  is not. Our labeling studies help in understanding the details of the four processes which occur (Scheme 1). Here we see that  $[\text{HSiO}]^-$  reacts initially by two pathways, one giving direct hydride transfer and the



Scheme 2

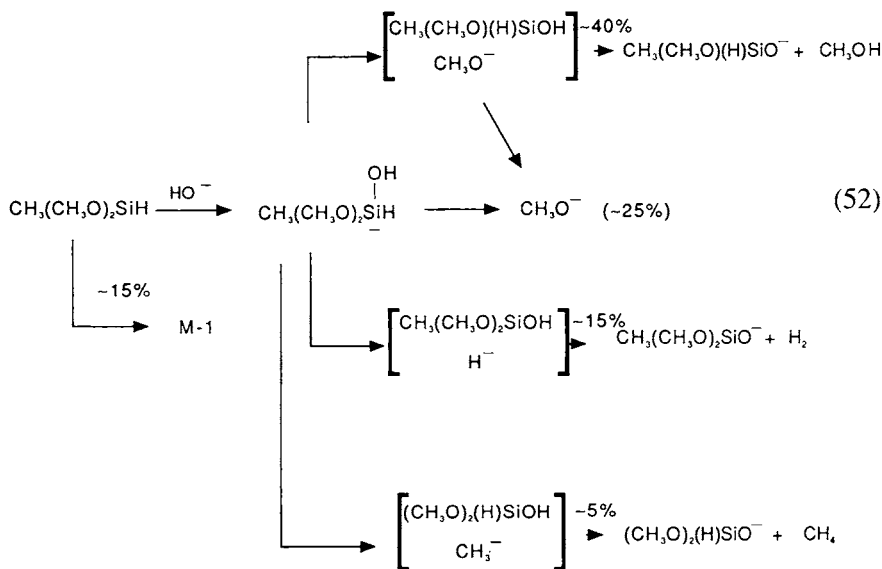


must form along the reaction pathway, but that both hydride and electron transfer must occur before its formation.<sup>37</sup> Finally, in reaction with hexafluorobenzene, other reaction pathways are traversed (eq. 51).<sup>37</sup> Here  $[\text{HSiO}]^-$  adds by ipso attack on carbon. The intermediate **5**



so formed then loses fluoride giving complex **6** in which fluoride reacts at silicon, thus giving a second complex **7**. Each of the products can easily be seen to arise from this second complex.

We have also studied<sup>34</sup> the chemistry of  $[\text{CH}_3\text{SiO}]^-$  and  $[\text{CH}_3\text{OSiO}]^-$ . Since they are so closely related to that of  $[\text{HSiO}]^-$ , the details of their characterization will not be given here. As part of this study, however, a careful evaluation of the reactions leading to various siloxides and the CID of some of them as precursors to  $[\text{RSiO}]^-$  species was carried out. These results have particular relevance to CID studies by Bowie and co-workers on other siloxides,<sup>79</sup> on other silicon-containing compounds,<sup>79,80</sup> and to various studies of ours in which cleavage reactions occur.<sup>30,81</sup> Five siloxides,  $(\text{CH}_3)_2(\text{CH}_3\text{O})\text{SiO}^-$  (**8**),  $(\text{CH}_3\text{O})_2(\text{H})\text{SiO}^-$  (**9**),  $(\text{CH}_3\text{O})_3\text{SiO}^-$  (**10**),  $\text{CH}_3(\text{CH}_3\text{O})(\text{H})\text{SiO}^-$  (**11**), and  $\text{CH}_3(\text{CH}_3\text{O})_2\text{SiO}^-$  (**12**), have been prepared by reaction of the appropriate methoxysilane and hydroxide.<sup>34</sup> Each has then been selected in the FA-SIFT and subjected to CID study. Equation 52



illustrates the complexities of the reaction between hydroxide and methyldimethoxysilane. Not only is there a direct proton abstraction channel, but three siloxides form from a common siliconate intermediate. The siloxides each arise from a reaction complex containing a strongly basic anion and a neutral silane. The proportion of siloxide products has been shown to be related to the basicity of the anion in the

reaction complex. Thus, in much the same way as in our alkane acidity studies<sup>30,41</sup> where a less basic group is cleaved in preference to a more basic one, methoxide is cleaved here in preference to hydride which is cleaved in preference to methide.

Collision-induced dissociation of the siloxides **8–12** can be understood in much the same way (products for each are given in Table 8).<sup>34</sup> Siloxide ions **8** and **11** will serve to illustrate the processes and principles which govern these dissociations. Typically, CID gives a reaction complex composed of a neutral Si=O compound and a basic

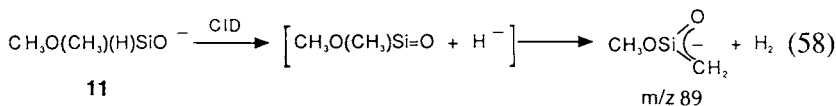
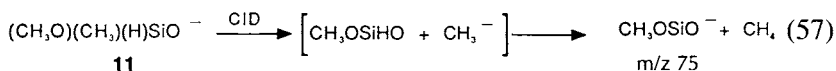
**Table 8.** Collision-Induced Decomposition of Siloxides **8–12**<sup>34</sup>

Reactant	Products (m/z)
$(\text{CH}_3)_2(\text{CH}_3\text{O})\text{SiO}^-$ ( <b>8</b> )	$\text{CH}_3\text{Si} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{CH}_2 \end{array}$ ( <b>73</b> ) $(\text{CH}_3)_2(\text{H})\text{SiO}^-$ ( <b>75</b> ) or $\text{CH}_3\text{SiO}_2^-$ ( <b>75</b> )
$(\text{CH}_3\text{O})_2(\text{H})\text{SiO}^-$ ( <b>9</b> )	$\text{CH}_3\text{OSiO}^-$ ( <b>75</b> ) $(\text{CH}_3\text{O})(\text{H})(\text{HO})\text{Si}^-$ ( <b>77</b> ) or $(\text{CH}_3\text{O})(\text{H})_2\text{SiO}^-$ ( <b>77</b> )
$(\text{CH}_3\text{O})_3\text{SiO}^-$ ( <b>10</b> )	$\text{CH}_3\text{OSiO}^-$ ( <b>75</b> ) $(\text{CH}_3\text{O})_2(\text{HO})\text{Si}^-$ ( <b>107</b> )
$(\text{CH}_3\text{O})(\text{CH}_3)(\text{H})\text{SiO}^-$ ( <b>11</b> )	$\text{CH}_3\text{SiO}^-$ ( <b>59</b> ) $^- \text{CH}_2\text{SiHO}$ ( <b>59</b> ) $\text{CH}_3(\text{H})_2\text{SiO}^-$ ( <b>61</b> ) or $\text{CH}_3(\text{H})(\text{HO})\text{Si}^-$ ( <b>61</b> ) $\text{CH}_3\text{OSiO}^-$ ( <b>75</b> ) $\text{CH}_3\text{OSi} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{CH}_2 \end{array}$ ( <b>89</b> )
$\text{CH}_3(\text{CH}_3\text{O})_2\text{SiO}^-$ ( <b>12</b> )	$\text{CH}_3\text{OSi} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{CH}_2 \end{array}$ ( <b>89</b> ) $\text{CH}_3(\text{CH}_3\text{O})(\text{HO})\text{Si}^-$ ( <b>91</b> ) or $\text{CH}_3(\text{CH}_3\text{O})(\text{H})\text{SiO}^-$ ( <b>91</b> )





shows that two products are formed from a complex of silaacetaldehyde and methoxide. These two isomers have been shown to be present using characterizing reagents. We cannot distinguish whether  $m/z$  61 is  $\text{CH}_3(\text{H})_2\text{SiO}^-$  or  $\text{CH}_3(\text{H})(\text{HO})\text{Si}^-$  or both, but suggest that ions of this type must arise in a process analogous to equation 55. Formation of the other two products is illustrated in equations 57 and 58. Both arise from different CID product complexes by proton abstraction.<sup>34</sup>



These examples of CID all indicate that, although these are high energy processes, they occur by rational paths similar to ones we have seen in cleavage reactions and in the formation of siloxides **8–12**. There is less specificity of product formation, however, because the energies involved in CID are greater than those associated with more regular chemical processes in the flowing afterglow.

Bowie and co-workers' CID studies, although of a wider scope than ours, draw similar conclusions.<sup>79</sup> Although we will not detail their work, a report of one of their recent studies will serve to demonstrate the importance of their contributions. The question of whether every reaction between a silane and a nucleophile must form a silicate intermediate has been addressed using CID techniques.<sup>82</sup> Methoxytrimethylsilane,  $(\text{CH}_3)_3\text{SiOCH}_3$ , has been reacted with both methoxide and deuterio-methoxide and ions corresponding to the  $m/z$  of the adducts have been trapped. These presumably could be mixtures of silicate and other species with the same  $m/z$ . O'Hair and Bowie suggest that other structures, especially ones where methoxide interacts with the hydrogen of one of the methyl groups, are possible. Subjecting such ions to CID study shows that by far most of the adduct ions are silicates, but that a small amount of other ions is present as well. Other studies by Bowie and co-workers have focused on the CID of silyl anions<sup>80</sup> and siloxides.<sup>79</sup>

## 5. CONCLUSIONS

This chapter is an attempt to demonstrate to silicon chemists the relevance of negative ion gas phase studies and the methods used in such studies. The author has tried to accomplish this by emphasizing general conclusions without too detailed discussion of actual experiments or instruments. The thermochemical aspects of negative ion gas phase work have been presented in the early part of the chapter. Reactivity studies demonstrating how some of the detailed thermochemical information is obtained follow as do studies which illustrate reactivity patterns for different silicon-containing species. Finally, various applications of the tandem FA-SIFT to silicon negative ion chemistry have been illustrated.

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