Gas-Phase Ion-Molecule Chemistry of Methoxy-Substituted Silanes: Collision-Induced Decomposition of Siloxide Ions Leading to Anions of Silaacetaldehyde and Methyl Silaformate

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Methoxy-substituted silanes react with hydroxide in a tandem flowing afterglow selected ion flow tube to give a number of siloxide ions. Five of these, $(CH_3)_2(CH_3O)SiO^-$, $(CH_3O)_2(H)SiO^-$, $(CH_3O)_3SiO^-$, $CH_3(CH_3O)(H)SiO^-$, and $CH_3(CH_3O)_2SiO^-$, have been submitted to collision-induced decomposition (CID) conditions. Three of these siloxides are suitable precursor ions for CH_3OSiO^- and CH_3SiO^- as well as an isomer of CH_3SiO^- which is the enolate of silaacetaldehyde. The chemistry of the siloxide ions has been studied by using N_2O, CO_2, CS_2, and COS as has that of many of the ions resulting from CID. The acidity of CH_3OSiO^- has been determined and compared with that of $HSiO^-$. The reported revision of the acidity of silaacetone takes account of up-to-date reference acidities.

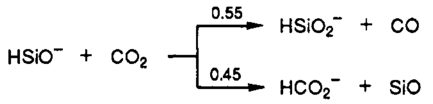
Introduction

Multiple bonding to silicon has been studied in considerable detail over the past few years.[1] Much of the impetus for this work came from kinetic studies of the pyrolysis of dimethylsilacyclobutane carried out in the late 1960s. These studies strongly suggested the intermediacy of dimethylsilene, $[(CH_3)_2Si{=}CH_2]$. Interest was further fueled by the desire to compare various multiply bonded silicon species with their carbon analogues (e.g., Si=C and Si=Si with C=C, Si=O with C=O, Si=N with C=N, etc.). Our current state of knowledge of such silicon species derives from two fronts: one directed at determining the spectroscopic properties of these species in matrix isolation;[1d] the other at preparing stable derivatives that are usually obtained by substituting the multiple bond with bulky groups.[1e] These studies have generally indicated that multiple bonds to silicon are thermodynamically stable, although less so than their carbon analogues, and that such bonds are quite reactive, more so than their carbon analogues.

Despite the intense activity on multiply bonded silicon species, there is little experimental information on simply substituted species. We have approached this problem by studying the gas-phase ion-molecule chemistry of substituted silicon anions whose conjugate acids are related to simple silicon species. For example, we have previously studied $SiCH^-$ and $HSiO^-$ because of their relationship to silaacetylene and silanone.[2,3] These two studies illustrate the approach we have taken as well as its advantages and limitations.

In studying the chemistry of $SiCH^-$, we have determined that the H is bonded to carbon rather than silicon and found that this ion reacts as a carbon-centered nucleophile.[2] One of the limitations of our gas-phase methods is illustrated in measuring the acidity of the parent conjugate acid. Although such a measurement is easily made, the identity of the neutral parent compound is not always clear since the flowing afterglow (FA) technique detects only ionic species. The parent of $SiCH^-$ could be either $HSi{\equiv}CH$, $H_2Si{=}C$, or $Si{=}CH_2$. High-level ab initio computations strongly suggest that the most stable isomer is $Si{=}CH_2$.[4]

Detailed studies of $HSiO^-$ have examined its fascinating reaction chemistry, where, for example, it reacts with CO_2 in both an oxidative and a reductive channel (eq 1).[3] In



$$HSiO^- + CO_2 \begin{cases} \xrightarrow{0.55} HSiO_2^- + CO & (1a) \\ \xrightarrow{0.45} HCO_2^- + SiO & (1b) \end{cases}$$

addition, we have been able to determine the heats of formation of both $HSiO^-$ and its conjugate acid. Here again, we have the limitation of not knowing the structure of the neutral, which could be either $H_2Si{=}O$ or HSiOH. The several computational studies published on these isomers suggest only very small energetic differences with HSiOH more stable by just a few kcal/mol.[3,5] Computations at a higher level indicate that $H_2Si{=}O$ is more stable than HSiOH by 2.7 kcal/mol [MP2/6-31G(d,p) geometries and MP4/MC-311G(d,p) energies corrected for zero-point vibrational energies].[6]

In the studies reported here, we have extended our $HSiO^-$ work to anions related to CH_3SiHO and $HSiO_2CH_3$, the silicon analogues of acetaldehyde and methyl formate, respectively. This study addresses questions about their synthesis by collision-induced decomposition (CID) of various methoxy-substituted siloxide ions, about their reactivity and structure, and about their thermochemistry.

Experimental Section

All experiments were carried out at room temperature in a flowing afterglow selected ion flow tube (FA-SIFT) which has been

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[1] *The Chemistry of the Functional Groups*: *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, R. I., Eds.; Wiley: New York, 1989. These two volumes, which have just been published, are likely to set the standard as a general reference work on organosilicon chemistry for years to come. More specific references to multiply bonded silicon species follow: (a) Raabe, G.; Michl, J. In *The Chemistry of the Functional Groups*: *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, R. I., Eds.; Wiley: New York, 1989; Chapter 17. (b) Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529. (c) Bertrand, G.; Trinquier, G.; Mazerolles, P. *J. Organomet. Chem. Libr.* **1981**, *12*, 1. (d) Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141. (e) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (f) Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *29*, 1.

[2] Damrauer, R.; DePuy, C. H.; Barlow, S. E.; Gronert, S. *J. Am. Chem. Soc.* **1988**, *110*, 2005. For initial observations of collisional activation in a SIFT instrument, see: Henchman, M.; Viggiano, A. A.; Paulson, J. F.; Freedman, A.; Wormhoudt, J. *J. Am. Chem. Soc.* **1985**, *107*, 1453.

[3] Gronert, S.; O'Hair, R. A.; Prodnuck, S.; Sülzle, D.; Damrauer, R.; DePuy, C. H. *J. Am. Chem. Soc.* **1990**, *112*, 997.

[4] Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M.; Apeloig, Y.; Karni, M.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 270.

[5] (a) Kudo, T.; Nagase, S. *Organometallics* **1986**, *5*, 1207. (b) Kudo, T.; Nagase, S. *Chem. Phys. Lett.* **1986**, *128*, 507. (c) Kudo, T.; Nagase, S. *J. Am. Chem. Soc.* **1985**, *107*, 2589. (d) Kudo, T.; Nagase, S. *J. Phys. Chem.* **1984**, *88*, 2833. (e) Kudo, T.; Nagase, S. *J. Organomet. Chem.* **1983**, *253*, C23. (f) Gordon, M. S.; George, C. *J. Am. Chem. Soc.* **1984**, *106*, 609.

[6] Gordon, M. S.; Peterson, L. A. *J. Phys. Chem.*, submitted.

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described in detail previously.[7] A brief description of the technique follows. The FA-SIFT consists of four sections: a source flow tube for ion preparation (A), an ion separation and purification region (B), a second flow tube for studying the chemical reactions of the selected ions (C), and finally an ion detection region (D). In the first flow tube (A) oxide ions (O^-) are prepared by electron ionization of small amounts of N_2O (0.01 Torr) entrained in a rapidly flowing (40 m/s) helium stream (0.4 Torr), and these are rapidly converted to hydroxide ions by hydrogen atom abstraction from 0.02 Torr of methane also entrained in the helium. Downstream various silanes are added through a moveable inlet, and rapid reactions ensue, producing a variety of ionic products.

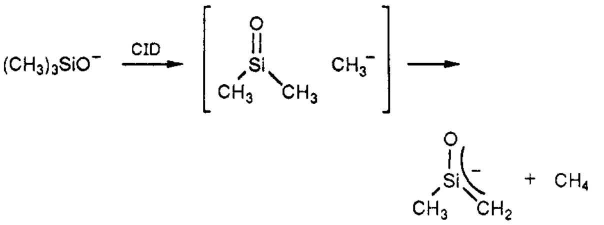
At the end of the first flow tube the ions are sampled through a 2-mm orifice into the ion separation region (B), and the helium and other neutrals are removed by pumping, while the ions are focused into a quadrupole mass filter by a series of electrostatic lenses. This SIFT quadrupole is tuned to an appropriate m/z, and the desired ion is injected into the second flow tube (C), where it is again entrained in helium (0.5 Torr). At the end of the second flow tube ions are sampled through a 0.5-mm orifice, mass analyzed, and detected by an electron multiplier.

To inject ions from the low-pressure (10^{-6} Torr) region of the SIFT quadrupole into the higher pressure region of the second flow tube, they must be extracted by an electrical potential. This potential imparts kinetic energy to the ions, which is removed by multiple collisions with the helium buffer gas. If this potential is made sufficiently high, ions can undergo collision-induced dissociation (CID) to form new ions. In a field-free region, the resulting ions subsequently undergo multiple collisions with helium and are usually cooled to room temperature before being allowed to react with neutral reagents. The injection potential leading to decomposition of ions is the potential difference between the ion source and the injector plate. The resulting exact kinetic energy of the ions is a sensitive function of a variety of factors and, thus, is not well characterized.

All reactions were studied at 300 K at a helium buffer gas pressure of 0.5 Torr and a flow of 250 STP $cm^3\ s^{-1}$. Branching ratios were determined as a function of reaction distance and are reported as extrapolations to zero reaction distance to eliminate any effects of differential diffusion among the ions and of secondary reactions. Gases were obtained from commercial sources and were of the following purities: He (99.995%), N_2O (99.99%), O_2 (99.95%), CH_4 (99.99%), CO_2 (99.5%), SO_2 (99.9%), and COS (97.7%). Other reagents also were obtained from commercial sources and were purified as necessary before use. The helium buffer gas was passed through a liquid nitrogen cooled molecular sieve trap before entering the flow tubes.

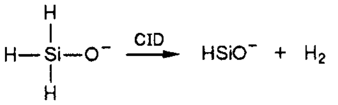
Results and Discussion

Many of the likely pathways for CID of siloxide ions have been recently explored by Squires, Bowie, and coworkers.[8,9] Squires seminal work carried out by FTMS techniques described the decomposition of $(CH_3)_3SiO^-$, which yielded silaacetone enolate and methane (eq 2), presumably following the path illustrated.[8] More recently, Bowie has described the CID behavior of a number of siloxides [$(CH_3)_3SiO^-$, $(CH_3)_2HSiO^-$, $(CH_3)_2(CH_3CH_2)SiO^-$, $(CH_3CH_2)_3SiO^-$, $(CH_3CH_2)_2HSiO^-$, $(CH_3)_2(CH_2{=}CHCH_2)SiO^-$, $(CH_3)_2(CH_2{=}CH)SiO^-$, and $(C_6H_5)_3SiO^-$].[9] In addition, ab initio computations on the silaacetone anion and CH_3SiO^- have been reported.[9]

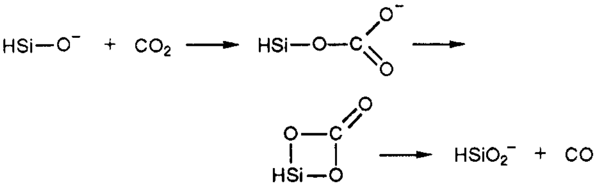


(2)

With our recent observation that CID experiments could be carried out in the flowing afterglow selected ion flow tube (FA-SIFT),[3] we realized that many of the tremendous variety of interesting ions that could be produced in the FA source could be collisionally decomposed and that subsequent reactions using conventional FA techniques could probe their identity and reactivity. Thus, FA-SIFT has a potentially significant advantage over other techniques since the chemistry of the ions produced by CID can be studied in detail, as our recent study of $HSiO^-$ illustrates very well. This anion has been prepared by CID of H_3SiO^- (eq 3). Its chemistry has been probed by using CO_2, COS, CS_2, SO_2, O_2, acetic acid, nitromethane, and hexafluorobenzene and is largely dominated by two factors: its high nucleophilic reactivity at oxygen (eq 1a) and its hydride-donating tendencies (eq 1b). A number of the reactions of $HSiO^-$, as well as those of $SiCH^-$, are reasonably explained by mechanisms involving four-membered intermediates (eqs 4 and 5).



$$H_3Si{-}O^- \xrightarrow{CID} HSiO^- + H_2 \qquad (3)$$



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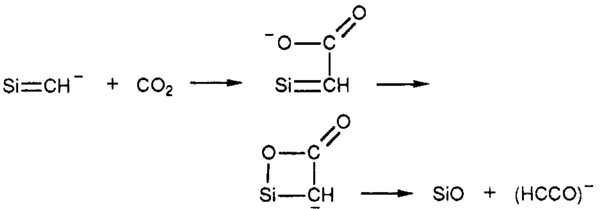

(5)

In this study we have further realized the potential of the CID FA-SIFT technique by examining the decomposition of several new siloxides. We also have examined the effect of methoxy substituents on silicon since Bowie and co-workers[11] had previously reported a number of interesting examples of ion–molecule chemistry involving methoxysilanes. Finally, we explore more complex silicon compounds having the potential for multiple reaction pathways.

Reactions of Methoxysilanes with Hydroxide: Siloxide Ion Formation. We have examined the reaction of hydroxide with trimethylmethoxysilane, dimethyldimethoxysilane, trimethoxysilane, and methyldimethoxy-

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(7) Van Doren, J. M.; Barlow, S. E.; DePuy, C. H.; Bierbaum, V. M. *Int. J. Mass Spectrom. Ion Proc.* **1987**, *81*, 85.

(8) Froelicher, S. W.; Freiser, B. S.; Squires, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 6863.

(9) O'Hair, R. A.; Bowie, J. H.; Currie, G J. *Aust. J. Chem.* **1988**, *41*, 57.

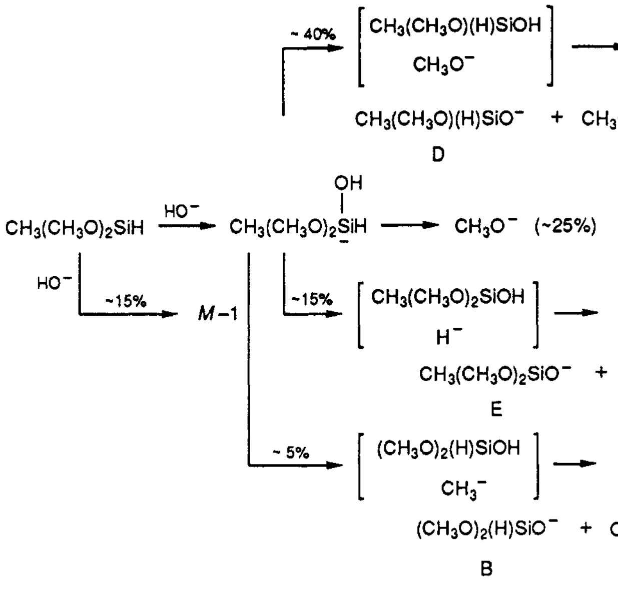
(10) We have used a bracket notation throughout this paper to represent ion–molecule product complexes. The more common notation of enclosing intermediates in brackets has not been used to avoid confusion. The sense of the text makes it clear when intermediate species are being represented in the equations. We have used the term "ion–molecule product complex" to describe those complexes formed as the result of either the decomposition of a siliconate or the CID of a siloxide. This terminology distinguishes such cases from collision complexes that result when a reactant ion and a neutral collide. We thank one of the referees for suggesting that we emphasize these differences.

(11) (a) Klass, G.; Trenerry, V. C.; Sheldon, J. C.; Bowie, J. H. *Aust. J. Chem.* **1981**, *34*, 519. (b) Hayes, R. N.; Bowie, J. H.; Klass, G. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1167.

Table I. Reactions of Hydroxide and Methoxysilanes

reactant	products
$(CH_3)_3SiOCH_3$	$M - 1$ (≈10%) CH_3O^- (≈55%) $(CH_3)_3SiO^-$ (≈25%) $(CH_3)_2(CH_3O)SiO^-$ (≈10%) (A)
$(CH_3)_2Si(OCH_3)_2$	$M - 1$ (≈15%) CH_3O^- (≈20%) $(CH_3)_2(CH_3O)SiO^-$ (≈50%) (A) $(CH_3)(CH_3O)_2SiO^-$ (≈15%) (E)
$(CH_3O)_3SiH$	$M - 1$ (≈10%) CH_3O^- (≈35%) $(CH_3O)_2(H)SiO^-$ (≈40%) (B) $(CH_3O)_3SiO^-$ (≈15%) (C)
$CH_3(CH_3O)_2SiH$	$M - 1$ (≈15%) CH_3O^- (≈25%) $CH_3(CH_3O)(H)SiO^-$ (≈40%) (D) $CH_3(CH_3O)_2SiO^-$ (≈15%) (E) $(CH_3O)_2(H)SiO^-$ (≈5%) (B)

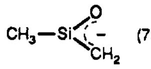
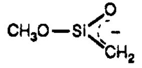
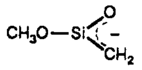
silane. The products from these reactions are compiled in Table I. Of particular importance to this work is the formation of various siloxide ions from these methoxysilanes. Siloxide ion formation is consistent with a mechanism previously suggested in which hydroxide adds to tetracoordinate silicon to form a pentacoordinate anionic intermediate (siliconate).[12] Since this is a highly exothermic addition,[13] the resulting intermediate cannot be stabilized by collision and fragments to give an ion–molecule product complex[10] of a tetracoordinate silanol and a basic anion (in these cases, methoxide, hydride, and/or methide). Before the basic anion can escape the ion–molecule product complex, it abstracts the SiO–H proton, giving a siloxide. Equation 6 illustrates the proposed pathways leading to the products for the most complex example we have studied, the reaction of methyldimethoxysilane and hydroxide.



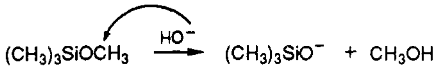
(6)

In eq 6 the three siloxides result from the same pentacoordinate intermediate, $[CH_3(CH_3O)_2(H)SiOH]^-$. This intermediate fragments to give ion–molecule product complexes of methylmethoxysilanol and methoxide, methyldimethoxysilanol and hydride, and dimethoxysilanol and methide ion. The three resulting siloxides are then formed in amounts at least partially controlled by the basicity of the anionic component of these ion–molecule product complexes. We have shown in studies on alkane acidities that the less basic anions are more readily cleaved from silicon;[12] here, in much the same way, the ion–molecule product complex containing methoxide is expected to predominate over that containing hydride over that containing methide as the branching ratios indicate. Such an explanation holds equally well for the other three reactions recorded in Table I.

Table II. Collision-Induced Decomposition of Siloxides A–E

reactant	products (m/z)
$(CH_3)_2(CH_3O)SiO^-$ (A)	 (73) $(CH_3)_2(H)SiO^-$ (75) or $CH_3SiO_2^-$ (75) [see text]
$(CH_3O)_2(H)SiO^-$ (B)	CH_3OSiO^- (75) $(CH_3O)(H)(HO)Si^-$ (77) or $(CH_3O)(H)_2SiO^-$ (77) [see text]
$(CH_3O)_3SiO^-$ (C)	CH_3OSiO^- (75) $(CH_3O)_2(HO)Si^-$ (107)
$(CH_3O)(CH_3)(H)SiO^-$ (D)	CH_3SiO^- (59) $^-CH_2SiHO$ (59) $CH_3(H)_2SiO^-$ (61) or $CH_3(H)(HO)Si^-$ (61) [see text] CH_3OSiO^- (75)  (89)
$CH_3(CH_3O)_2SiO^-$ (E)	 (89) $CH_3(CH_3O)(HO)Si^-$ (91) or $CH_3(CH_3O)(H)Si^-$ (91) [see text]

In each of the four reactions with hydroxide, the product that arises from methoxide cleavage might result from an alternate mechanism to the one just proposed. S_N2 reaction of hydroxide at the methyl of the methoxy groups would lead to siloxide product directly (eq 7). We have



$$(CH_3)_3SiOCH_3 \xrightarrow{HO^-} (CH_3)_3SiO^- + CH_3OH \quad (7)$$

studied this possibility by using ^{18}O-labeled HO^- in reactions with $(CH_3)_2Si(OCH_3)_2$ and $(CH_3)_3SiOCH_3$ and have evidence that both S_N2 reaction and association to a pentacoordinate silaconate are occurring simultaneously, although this cannot be quantified.

In summarizing the reactions of the methoxysilanes with hydroxide, the predominant reaction path involves the formation of a pentacoordinate silicon anion (siliconate) from which methoxide formation results. With the exception of the M-1 products (10–15)% and that amount of S_N2 reaction occurring, the rest of the products form from their respective siliconates.

Collision-Induced Decomposition of Siloxides: Product Identification Studies. Siloxide ions A–E (Table I) undergo collision-induced decomposition (CID) to the products given in Table II.

An ion such as A potentially can decompose in several ways. We suggest that the m/z = 73 ion that forms is silaacetone enolate resulting from a complex of silaacetone and methoxide by a process analogous to that illustrated in eq 2. Four m/z = 75 possibilities exist; two of these could result from a complex of methyl silaacetate and methide (eq 8). In one, CH_3OSiO^- could form when methide attacks the methyl group attached to silicon thus forming ethane (eq 8a). The other decomposition could lead to silaacetate and ethane from methide attack at the

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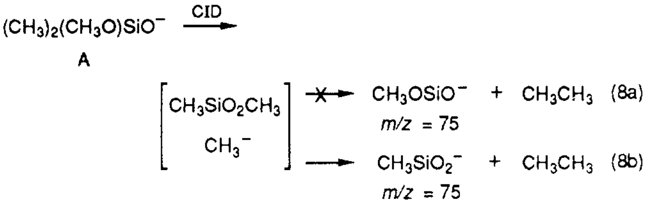
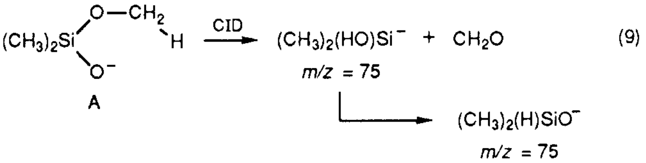
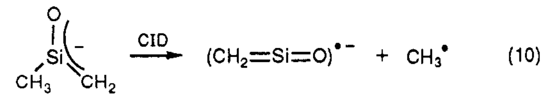
(12) DePuy, C. H.; Gronert, S.; Barlow, S. E.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1989**, *111*, 1968.

(13) Damrauer, R.; Burggraf, L. W.; Davis, L. P.; Gordon, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 6601.



methyl of methoxy bound to silicon (eq 8b). A third *m/z* = 75 ion could result from A by a cyclic decomposition, and the last *m/z* = 75 ion could arise by a 1,2-proton shift of $(CH_3)_2(HO)Si^-$ (eq 9). It is difficult to distinguish these structural possibilities since only a small amount of the *m/z* = 75 ion is produced in the presence of much larger amounts of the undecomposed siloxide and the silaacetone enolate as well as smaller amounts of several other ions. We have narrowed a structural assignment of *m/z* = 75 to either $(CH_3)_2(H)SiO^-$ or $CH_3SiO_2^-$ by allowing the reaction mixture to react with CO_2, N_2O, and CS_2. We note that the *m/z* = 75 signal is not diminished by the introduction of N_2O, suggesting that $(CH_3)_2(HO)Si^-$ is not present in significant amounts.[14] Since we had previously reacted only simple silyl anions with N_2O, we thought it prudent to generate $(CH_3)_2(CH_3O)Si^-$ (from $[(CH_3)_2(CH_3O)Si]_2$ and amide) and to react this ion with N_2O. We have done so and confirm that silyl anions, even those with a methoxy substitution, react with N_2O to give the corresponding siloxide. Reaction of the *m/z* = 75 ion with CS_2 gives a *m/z* = 91 ion. Since we will shortly show that CH_3OSiOS^- (*m/z* = 107) is a characteristic product of CS_2 and CH_3OSiO^-, the latter ion can be eliminated. Having independently demonstrated that $CH_3SiO_2^-$ reacts with CS_2 to give CH_3SiOS^- (*m/z* = 91), we see that $(CH_3)_2(H)SiO^-$ and $CH_3SiO_2^-$ could both give *m/z* = 91 product ions. Finally, reaction of *m/z* = 75 with CO_2 leads to an adduct, which is a reaction characteristic of siloxides and, we believe, silaacetates (see eq 18). Thus, given the experimental limitations just discussed, we are unable to further distinguish the *m/z* = 75 ion; it is either $(CH_3)_2(H)SiO^-$, $CH_3SiO_2^-$, or a mixture of the two. Another interesting ion, *m/z* = 58, is observed under higher energy decomposition conditions. This may be the radical anion of silaketene formed by the decomposition of silaacetone enolate as shown in eq 10. It is possible that decomposition of the enolate gives a complex of methide and silaketene. Because the methide electron is only weakly bound (the electron affinity of methyl radical is 1.8 kcal/mol),[15] electron transfer to the ketene could readily occur. It is, however, also possible that the silaacetone enolate could decompose directly to the products shown.

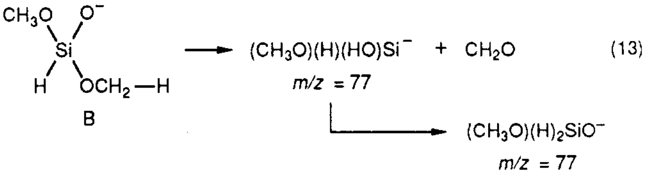




The decomposition of B gives two products (Table II). If complexes formed under CID conditions behave in a manner similar to the ion–molecule product complexes formed in the reactions of methoxysilanes and hydroxide, then CH_3OSiO^- more likely results from a complex of methyl silaformate and methoxide (eq 11) than from one of the dimethylsilacarbonate and hydride (eq 12). The *m/z* = 77 ion results from a cyclic extrusion of formaldehyde with $(CH_3O)(H)(HO)Si^-$ and/or $(CH_3O)(H)_2SiO^-$ resulting (eq 13). We have examined the structure of the *m/z* = 77 ion, but unlike the case of eq 9, we cannot distinguish between the silyl anion and siloxide structures. Reaction with CO_2 and CS_2 give products consistent with a silyl anion formulation, but reaction with N_2O gives only a few counts of an anion with an *m/z* corresponding to the expected siloxide product.

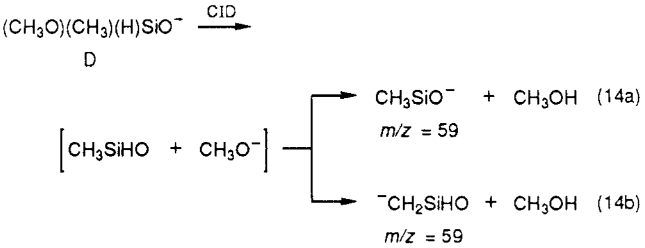
$$\underset{\text{B}}{(CH_3O)_2(H)SiO^-} \xrightarrow{\text{CID}} [CH_3OSiHO + CH_3O^-] \rightarrow \underset{m/z\,=\,75}{CH_3OSiO^-} + CH_3OH \quad (11)$$

$$\underset{\text{B}}{(CH_3O)_2(H)SiO^-} \xrightarrow{\text{CID}} [(CH_3O)_2Si{=}O + H^-] \rightarrow \underset{m/z\,=\,75}{CH_3OSiO^-} + H_2 + CH_2O \quad (12)$$



Ion C decomposes under CID conditions to CH_3OSiO^- and $(CH_3O)_2(HO)Si^-$ (Table II) with varying, but usually small, amounts of SiO_2^- depending on CID conditions. Under favorable circumstances CH_3OSiO^- can be prepared in 10-fold excess over the other products and is suitably pure for reactivity studies. We have also cleanly generated CH_3OSiO^- from $(CH_3O)_3SiO^-$ that has been obtained by reaction of tetramethoxysilane and hydroxide.

CID of $CH_3(CH_3O)(H)SiO^-$ (D) leads to the product shown in Table II. A mixture of two *m/z* = 59 ions arises from an ion–molecule product complex of silaacetaldehyde and methoxide (eq 14). In one case, the methoxide abstracts a silaacyl hydrogen giving CH_3SiO^- (eq 14a). In the other case, a proton is abstracted from C–H giving $^-CH_2SiHO$ (eq 14b). As will be shortly demonstrated, these two isomers can be distinguished on the basis of their reaction chemistry. In addition, the ion at *m/z* = 61 forms in quite large amounts. It could be either $CH_3(H)_2SiO^-$ or $CH_3(H)(HO)Si^-$, resulting from processes analogous to eq 9. The complexity of the reaction mixture hindered our effort to determine the structure of the *m/z* = 61 ion. Other ions are formed in smaller amounts, including the *m/z* = 75 ion, which can form as shown in eq 15, and the



$$\underset{\text{B}}{(CH_3O)(CH_3)(H)SiO^-} \xrightarrow{\text{CID}} [CH_3OSiHO + CH_3^-] \rightarrow \underset{m/z\,=\,75}{CH_3OSiO^-} + CH_4 \quad (15)$$

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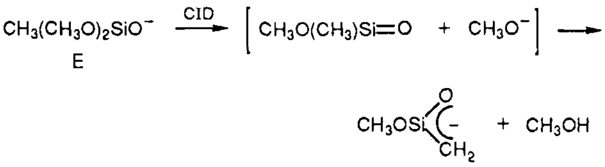
(14) Damrauer, R.; DePuy, C. H. *Organometallics* **1984**, *3*, 362.

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

m/z = 89 ion, the enolate of methyl silaacetate, which likely forms from the ion–molecule product complex containing hydride.

Ion E decomposes to give m/z = 89 and 91. The first of these forms from an ion–molecule product complex of methyl silaacetate and methoxide (eq 16); the second could be produced by a cyclic extrusion process like that shown in eqs 9 and 13, but, as before, could undergo a 1,2-proton shift giving the silyl ion. Once again, an unambiguous structural assignment has been impossible, and these structural possibilities have not been distinguished.

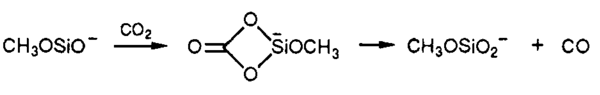


(16)

The principles governing product formation in collision-induced decompositions have similarities to those governing the reactions of the methoxysilanes and hydroxide (eq 6). Decompositions occur giving ion–molecule product complexes that collapse to the observed ions. The nature of our CID experiments makes it not only difficult to know the amount of energy supplied in a typical collision, but also impossible to measure reasonable branching ratios. Despite the energetic nature of these processes, we suspect that those ion–molecule product complexes containing less basic anions are favored and at least partially control the CID product distributions.

Anions Related to Silaacetaldehyde and Methyl Silaformate. In our earlier study the exceptional reactivity of $HSiO^-$ was probed.[3] Because of this we sought to examine the effect of various substituents on the reactivity of analogous ions. We have already indicated that CH_3OSiO^- can be prepared cleanly; in addition, mixtures of CH_3SiO^- and $^-CH_2SiHO$ (eq 14) have proved suitable for reactivity studies. In general, the reactivity of both CH_3OSiO^- and CH_3SiO^- are similar to that of $HSiO^-$. Perhaps as interesting is the chemistry involving mixtures of CH_3SiO^- and $^-CH_2SiHO$, which can be distinguished by their different reactivity.

A. Chemistry of CH_3OSiO^-. Because CH_3OSiO^- can be cleanly generated, we will concentrate on its chemistry first. Its reactivity differs from $HSiO^-$ in one major aspect since it cannot be a hydride donor; otherwise, it is quite similar to $HSiO^-$. Its reaction with CO_2 gives $CH_3OSiO_2^-$ and CO (eq 17). This reaction presumably occurs through a cyclic intermediate as shown.



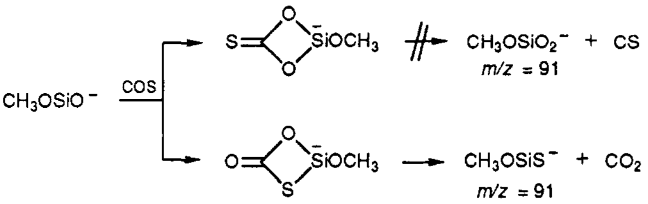
(17)

We earlier demonstrated with $HSiO^-$ that the analogous reaction pathway leading to $HSiO_2^-$ and CO was more complicated than it appeared. Thus, ^{18}O-labeled $HSiO^-$ gave both labeled and unlabeled $HSiO_2^-$, demonstrating that the proposed cyclic intermediate is formed reversibly from the initial adduct.[3] Although we have not carried out such labeling experiments with CH_3OSiO^-, there is no reason to doubt that this ion also reversibly forms its cyclic intermediate. We have also found a secondary pathway in the CH_3OSiO^- plus CO_2 reaction that was not seen with $HSiO^-$ (eq 18). Here,

$$\underset{}{CH_3OSiO^-} \xrightarrow{CO_2} \underset{m/z = 91}{CH_3OSiO_2^-} \xrightarrow{CO_2} \underset{m/z = 135}{CH_3OSiO_2CO_2^-} \qquad (18)$$

CH_3OSiO_2 reacts to give a CO_2 adduct. As we will see shortly, this reaction allows us to distinguish between the isomeric ions $CH_3OSiO_2^-$ and CH_3OSiS^-.

Reaction with COS can lead to two possible cyclic intermediates and two isomeric anions (eq 19). Thus, the loss of CS from one of these could lead to $CH_3OSiO_2^-$ while CO_2 loss from the other intermediate could lead to an isomeric ion, CH_3OSiS^-. On the basis of branching ratios in the reaction of $HSiO^-$ and COS, we would expect CH_3OSiS^- to predominate (in the $HSiO^-$ reaction $HSiS^-$ is found in 65% yield, while only traces of $HSiO_2^-$ are detected). In the case at hand, reaction with CO_2 (eq 20)

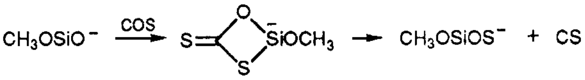


(19)

$$\underset{m/z\,=\,91}{CH_3OSiS^-} \xrightarrow{CO_2} \underset{\text{no adduct at }135}{CH_3OSiOS^- + CO} \qquad (20)$$

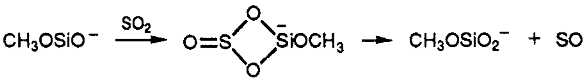
yields CH_3OSiOS^- with no detectable amount of the CO_2 adduct of $CH_3OSiO_2^-$. Another channel open in the $HSiO^-$ reaction (15%) has not bee seen with the CH_3OSiO^-, since CH_3OSiOS^- derived by CO loss from the lower cyclic intermediate in eq 19 has also not been detected.

Reaction between $HSiO^-$ and CS_2 gives two products, HCS_2^- (70%) and $HSiOS^-$ (30%). Since hydride donation from CH_3OSiO^- is impossible (as in the CO_2 example), it is not surprising that only CH_3OSiOS^- is found as the product in eq 21.



(21)

Reaction of CH_3OSiO^- with SO_2 also gives a single product, $CH_3OSiO_2^-$, although, on the basis of $HSiO^-$, we might also have expected a small amount of SO_2^-. We propose that $CH_3OSiO_2^-$ forms through the cyclic intermediate shown in eq 22. Because no electron transfer to SO_2 occurs, the electron affinity of CH_3OSiO^- is greater than that of $HSiO^-$ (whose upper limit is 1.1 eV).[3] This is, perhaps, not surprising since a methoxy would likely better stabilize an anion than a hydrogen substituent.

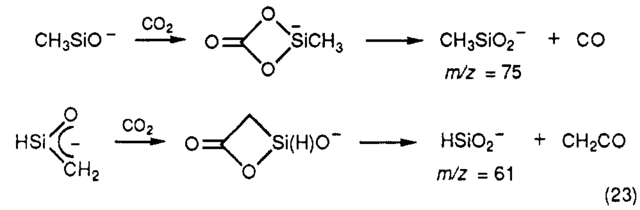


(22)

Finally, we have found that CH_3OSiO^- does not react with O_2, in contrast to $HSiO^-$, which gives SiO_2^- and $HSiO_2^-$.

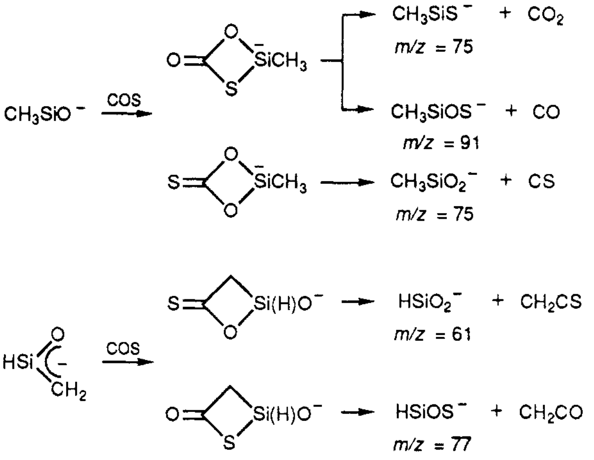
B. Chemistry of CH_3SiO^- and $^-CH_2SiHO$. In the CID of $CH_3(CH_3O)(H)SiO^-$ (D), we indicated that the two ions with m/z = 59 are formed. These were assigned the structures of CH_3SiO^- and $^-CH_2SiHO$. Their ratio (usually about 2:1) varies with injection conditions as does that between m/z = 59 and the other products. We have been unable to find conditions where the m/z = 59 signal is significantly greater than that of m/z = 61. Thus, although we are certain that the m/z = 59 signal is a mixture of two isomers, we were hampered in studying their detailed chemistry. Nevertheless, we have used CO_2, COS, and CS_2 (eqs 23–25) to probe the m/z = 59 isomer mixture.

Reaction with CO_2 is expected to give different products with the two isomers (eq 23), $CH_3SiO_2^-$ for CH_3SiO^- and $HSiO_2^-$ for $CH_2{=}Si(H)O^-$. Because $CH_3SiH_2O^-$ (m/z = 61) is present in the starting reaction mixture, we can

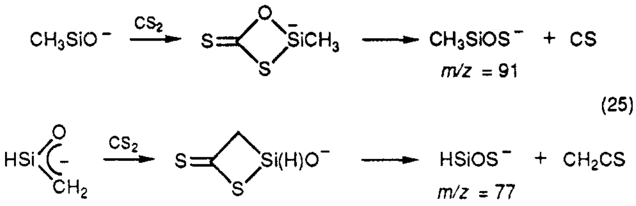


(23)

demonstrate only an increase in the m/z = 61 signal upon reaction with CO_2. However, COS and CS_2 give a clearer demonstration that the two isomers are present. The proposed cyclic intermediates, the products, and their m/z are shown in eqs 24 and 25. In the COS reaction, new



(24)



(25)

signals at m/z = 75 and 77 are found as well as increased signals at m/z 61 and 91 (the precursor ion D has a m/z = 91). In the CS_2 reaction, a new signal at 77 is detected, and the m/z = 91 signal increases as well.

Some computational work has been reported on CH_3SiO^- by Bowie and co-workers.[9] They reported a structure at the 6-31G* level that is similar to its carbon analogue, the acetyl anion. Since our experimental studies have indicated the presence of at least one other isomer of this ion, we have also undertaken a computational study to examine it as well as other possible isomers in further detail. These results will be reported at a later time.

Thermochemistry. We have successfully determined the proton affinity of CH_3OSiO^- but not of CH_3SiO^-. Thus, CH_3OSiO^- has been reacted with standard acids, and its acidity bracketed between those of CH_3CH_2CHO ($\Delta G°_{acid}$ = 359 kcal/mol) from which it abstracts a proton and $[(CH_3)_3Si]_2NH$ ($\Delta G°_{acid}$ = 353 kcal/mol) from which it does not. The parent compound of CH_3OSiO^- (CH_3OSiOH or CH_3OSiHO) then has $\Delta G°_{acid}$ = 356 ± 4 kcal/mol. We have reported the same acidity for $HSiO^-$, although the error limits for that determination were considerably greater (±8 kcal/mol). Without knowing with certainty the structures of the parent of either $HSiO^-$ or CH_3OSiO^-, it is premature to discuss the identical values of their acidities. With the completion of detailed computational studies, however, these acidities should derive a greater significance. Unfortunately, the complexity of the CH_3SiO^- and $^-CH_2SiHO$ reaction mixture has foiled attempts to determine the proton affinity of either component.

We have also checked Squires' earlier report of the acidity of silaacetone[8] bracketing its acidity between that of CH_3CHO ($\Delta G°_{acid}$ = 359 kcal/mol) and CF_3CH_2OH ($\Delta G°_{acid}$ = 354 kcal/mol). Its acidity is then 356 ± 4 kcal/mol, which is 2 kcal/mol less than Squires' report. This difference is based not on any experimental differences between our groups but rather on our use of newly published, updated values for the acidities in question. During the 5-year period since Squires' paper, the reported acidity of acetone has not changed while that of silaacetone has decreased as a result of updating of the values of some of the standard acids. Silaacetone, therefore, is about 5 kcal/mol more acidic than its carbon analogue. Interestingly, this is by far the smallest difference between carbon and silicon analogues of which we are aware.[16]

Other Reactions. To help us determine the structural characteristics of several ions that we obtained in the HO^- reactions, we have examined the reactivity with several of the neutral reagents used previously for this purpose. For example, we have established that ion E (m/z = 121) in Table I (eq 6) is $CH_3(CH_3O)_2SiO^-$ by its reaction (after SIFT selection) with CO_2 and COS (eqs 26 and 27). These

$$CH_3(CH_3O)_2SiO^- \xrightarrow{CO_2} CH_3(CH_3O)_2SiOCO_2^- \quad (26)$$

$$CH_3(CH_3O)_2SiO^- \xrightarrow{COS} CH_3(CH_3O)_2SiS^- + CO_2 \quad (27)$$

assignments are consistent with previous results showing that siloxides react with CO_2 to form adducts and with COS to form thiosiloxides. We have used CO_2 and CS_2 to assign structures A–D in a similar way. Recognizing that $(CH_3O)_2(H)SiO^-$ (B) and $CH_3(CH_3O)(H)SiO^-$ (D) might be their silyl anion isomers, $(CH_3O)_2(HO)Si^-$ and $CH_3(CH_3O)(HO)Si^-$, respectively, we have demonstrated that there is no reaction of D with N_2O, indicating that no silyl anion is present, at least in this case.

Finally, we have briefly considered the $M - 1$ product of eq 6, which on the basis of our work on methylsilanes[17] could be either the silyl anion from Si–H abstraction or the α-silyl carbanion from CH_2–H abstraction. Reaction of the M-1 anion with CO_2 gave $(CH_3O)_2(H)SiO^-$, a product consistent with an α-silyl carbanion formulation (eq 28).

$$CH_3(CH_3O)_2SiH \xrightarrow{HO^-} (CH_3O)_2(H)SiCH_2^- \xrightarrow{CO_2} (CH_3O)_2(H)SiO^- + CH_2{=}C{=}O \quad (28)$$

Acknowledgment. We gratefully acknowledge support of the National Science Foundation (Grant Number CHE-8615808) and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. A, 125518-33-4; B, 125495-76-3; C, 125495-77-4; D, 125495-78-5; E, 125495-79-6; $(CH_3)_3SiOCH_3$, 1825-61-2; $(CH_3)_2Si(OCH_3)_2$, 1112-39-6; $(CH_3O)_3SiH$, 2487-90-3; $CH_3(CH_3O)_2SiH$, 16881-77-9; HO^-, 14280-30-9; CH_3OSiO^-, 92622-86-1; CH_3SiO^-, 119703-47-8; $^-CH_2SiHO$, 125495-80-9; silaacetone, 47956-45-6.

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(16) Several comparisons can now be made between the acidity of a carbon compound and its silicon analogue. Among these, for example, are neopentane and tetramethylsilane, which differ in acidity by about 18 kcal/mol (see: DePuy, C. H.; Gronert, S.; Barlow, S. E.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1989**, *111*, 1968. Wetzel, D. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1988**, *110*, 8333), and isobutene and dimethylsilene, which differ by about 33 kcal/mol (see: Lias, S. G.; Bartmess, J. E.; Holmes, J. L.; Levin, R. D.; Liebman, J. F.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1. Damrauer, R.; DePuy, C. H.; Davidson, I. M. T.; Hughes, K. H. *Organometallics* **1986**, *5*, 2050).

(17) Damrauer, R.; Kass, S. R.; DePuy, C. H. *Organometallics* **1988**, *7*, 637.