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Gas-Phase Reactions of Anions with Substituted Silanes

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Abstract: The gas-phase reactions of fluoride, amide, hydroxide, and methoxide ions with a variety of substituted silanes have been studied by the flowing afterglow technique. Fluoride reacts readily with trimethylsilyl derivatives to displace benzyl, alkenyl, and alkynyl anions. These reactions have also been used to generate specific structural isomers ($CH_3C{\equiv}C^-$ and $CH_2{=}C{=}CH^-$). Anions more basic than phenide ion cannot be produced in this manner, and their parent trimethylsilanes interact with fluoride by more complex mechanisms. Amide, hydroxide, and methoxide ions react with substituted trimethylsilanes by both displacement and proton abstraction whenever an acidic hydrogen is present; in the absence of displaceable groups and acidic hydrogens, the reactions of amide, hydroxide, and methoxide parallel those of the fluoride ion.

Introduction

Interest in the gas-phase chemistry of anions, and in particular of organic anions, has increased in recent years, spurred in part by the potential application of negative ion chemical ionization mass spectrometry. Numerous studies with mass spectrometers[1,2] and ion cyclotron resonance spectrometers[3,4] have appeared. We have been using a flowing afterglow system for experiments of this kind.[5,6]

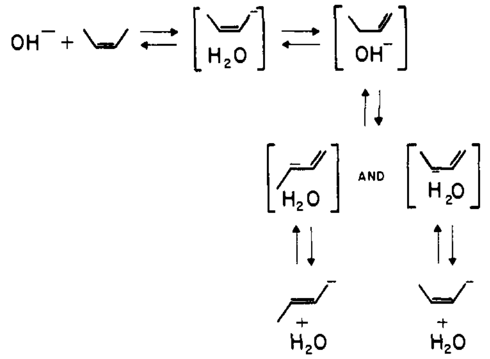
One immediate problem concerns methods for the formation of carbanions in the gas phase, since only a relatively few anions can be formed efficiently by electron capture. As a consequence most organic anions are generated by proton transfer from a neutral organic compound by a strong gas-phase base such as CH_3O^-, OH^-, or NH_2^-. In many cases this is an efficient and unambiguous method and, when applicable, is clearly the method of choice. As our studies have become more sophisticated, however, it has become apparent that proton transfer is not always a "simple" reaction and that the anions formed by such reactions do not always have the expected structure. We were therefore interested in developing a new method for the generation of gas-phase carbanions which would be more specific and which might overcome some of the problems of anion formation by proton transfer.

These problems are of at least three types. In the first place, even simple organic molecules may have more than one acidic site, and proton abstraction may give rise to a mixture of isomers. For example, we found[5] that proton abstraction by OH^- or NH_2^- from methylacetylene gives rise to a mixture of the propargyl and methylacetylide anions in which the former, although clearly of higher energy, predominates (eq 1). Even in as simple an alkene

$$\begin{aligned} OH^- + CH_3C{\equiv}CD &\xrightarrow{>60\%} {}^-CH_2C{\equiv}CD + H_2O \\ &\xrightarrow{<40\%} CH_3C{\equiv}C^- + HOD \end{aligned} \qquad (1)$$

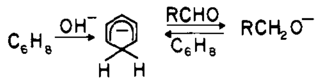
as 2-pentene there are different allylic positions from which proton abstraction is possible. In order to study such isomeric ions independently, we needed another, more specific method of carbanion formation.

A second difficulty in carbanion generation by proton abstraction is that ions of rearranged structure may result even from symmetrical neutral precursors.[5,7] This occurs because the carbanion and the neutral molecule produced do not always separate immediately, and reprotonation and reabstraction may occur. An example is proton abstraction from *cis*-2-butene by hydroxide ion. The cis anion can be reprotonated to 1-butene within the initial ion dipole complex; reabstraction can lead to either the cis or trans anion (eq 2). In this way proton abstraction from either *cis*- or *trans*-2-butene by hydroxide ion can lead to a mixture of the cis and trans anions.



(2)

Finally, for many experiments, it may be inconvenient to have present a large excess of acidic hydrocarbon, as it must be if it is to serve as the precursor to the carbanion. For example, cyclohexadiene anion can serve as a useful gas-phase hydride donor, reducing some aldehydes.[8] However, the alkoxide ion product can react with the initial diene to regenerate the cyclohexadiene anion (eq 3), greatly complicating the kinetic analysis.



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In this paper[9] we will describe a new method for the efficient generation of carbanions by the displacement reaction of fluoride ion on substituted trimethylsilanes. A number of different carbanions can be generated in this way, including alkenyl, alkynyl, and benzyl anions. The corresponding reactions of amide, hydroxide, and methoxide ions with substituted silanes will also be discussed; these reactions are less efficient for specific ion formation but represent mechanistically interesting chemistry.

Experimental Section

Our experiments were performed in a flowing afterglow system,[10] the details of which were described previously.[11] The reaction vessel is a 100

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(1) Kebarle, P. *Ann. Rev. Phys. Chem.* **1977**, *28*, 445–476.

(2) Jennings, K. R. *Mass Spectrom.* **1977**, *4*, 203–216.

(3) Bartmess, J. E.; McIver, R. T., Jr. *Gas Phase Ion Chem.* **1979**, *2*, 87–121.

(4) Nibbering, N. M. M. *NATO Adv. Study Inst. Ser., Ser. B* **1979**, *40*, 165–197.

(5) Stewart, J. H.; Shapiro, R. H.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1977**, *99*, 7650–7653.

(6) Schmitt, R. J.; Bierbaum, V. M.; DePuy, C. H. *J. Am. Chem. Soc.* **1979**, *101*, 6443–6445.

(7) DePuy, C. H.; Bierbaum, V. M.; King, G. K.; Shapiro, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 2921–2922.

(8) DePuy, C. H.; Bierbaum, V. M.; Schmitt, R. J.; Shapiro, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 2920–2921.

(9) For previous work in this area: DePuy, C. H.; Bierbaum, V. M.; Flippin, L. A.; Grabowski, J. J.; King, G. K.; Schmitt, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 6443.

(10) Ferguson, E. E.; Fehsenfeld, F. C.; Schmeltekopf, A. L. *Adv. At. Mol. Phys.* **1969**, *5*, 1–56.

(11) Bierbaum, V. M.; DePuy, C. H.; Shapiro, R. H.; Stewart, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4229–4235.

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× 7.6 cm i.d. stainless steel cylinder through which helium buffer gas flows at pressures near 0.4 torr and velocities of about 8000 cm s^{-1}. At the upstream end of the reaction tube the NH_2^- reagent ion is generated by the addition of small flows of NH_3 past an electron gun. Some OH^- impurity is always observed when NH_2^- is generated. F^- is generally produced by electron impact on NF_3 in the flow tube. However for some experiments where excess electrons or the NF_3 precursor presented problems, fluoride ion was produced in a low-pressure electron impact source, mass selected by a quadrupole mass filter, and injected into the flow tube through a venturi injector. The full description of the SIFT modification[12] of our flowing afterglow apparatus will appear in a later publication. OH^- is made by the addition of small flows of N_2O and CH_4 past the electron gun. CH_3O^- is produced either by an elimination reaction of NH_2^- with 1,2-dimethoxyethane or, more cleanly, by dissociative electron attachment to methyl nitrite. The anions generated in this manner are then collisionally relaxed by the helium buffer gas before reaction with the trimethylsilyl derivatives, which are added to the plasma through one of the downstream inlet ports or through the moveable inlet. Most of this reaction mixture is exhausted by the pumping system, but a small fraction of the ions are sampled, analyzed with a quadrupole mass filter, and counted by an electron multiplier.

For these experiments, the helium flow rate and density were approximately 180 STP $cm^3\ s^{-1}$ and $10^{16}\ cm^{-3}$, respectively. Gas purities were helium (99.995%), ammonia (99.999%), nitrous oxide (99.0%), methane (99.0%), and nitrogen trifluoride (97.5%).

Most of the silylated organic compounds were used as obtained from Petrarch Systems. *cis*- and *trans*-1-(trimethylsilyl)-2-butene were prepared essentially by the method of Slutsky and Kwart.[13] Thus the reaction of trimethylsilyl chloride with crotylmagnesium bromide afforded a mixture of (trimethylsilyl)butenes in high yield; however, the predominant isomer in the mixture was 3-(trimethylsilyl)-1-butene. This mixture was conveniently pyrolyzed on glass beads at 510 °C to yield a new mixture consisting of 48% *trans*- and 45% *cis*-1-(trimethylsilyl)-2-butene with only 7% of the unwanted isomer. After GC separation on a 10 ft × $^1/_4$ in. ODPN column (15% on 80/100 chrom P) at 80 °C, *cis*-1-(trimethylsilyl)-2-butene was obtained in ≥98% purity and the trans isomer in 86% purity (contaminated with 14% of 3-(trimethylsilyl)-1-butene). 1-(Trimethylsilyl)propyne, 1-(trimethylsilyl)-1-butyne, and 1-(trimethylsilyl)-1-hexyne were prepared by the reaction of methyllithium with the appropriate alkyne followed by the addition of trimethylsilyl chloride.[14] 3-(Trimethylsilyl)propyne was prepared from the Grignard reagent of 3-bromopropyne plus trimethylsilyl chloride.[13] There is an error in the published procedure,[13] omitting the anhydrous mercuric chloride which is required to catalyze this reaction. This method gave an eight to one mixture of 3-(trimethylsilyl)propyne and (trimethylsilyl)allene following distillation and was used at that level of purity. Benzyltrimethylsilane and phenyltrimethylsilane were made by the reaction of trimethylsilyl chloride with benzylmagnesium bromide and phenyllithium, respectively.

Results and Discussion

Table I summarizes the gas-phase reactions of fluoride ion with a variety of substituted trimethylsilanes. Rapid reaction of fluoride ion with allyltrimethylsilane generates predominantly the allyl anion (eq 4); a small amount of proton abstraction also occurs.

$$F^- + (CH_3)_3SiCH_2CH{=}CH_2 \rightarrow {}^-CH_2CH{=}CH_2 + (CH_3)_3SiF \quad (4a)$$

$$\rightarrow (CH_3)_3Si\overset{-}{C}HCH{=}CH_2 + HF \quad (4b)$$

The driving force for this reaction presumably is the formation of the extremely strong silicon–fluorine bond (154 kcal/mol)[15] which compensates for the conversion of a high electron affinity radical [EA(F) = 79.5 kcal/mol][16] to one with low electron affinity [EA($CH_2CH{=}CH_2$) ≈ 10–13 kcal/mol];[17,18] based on the value $D[(CH_3)_3Si{-}CH_3]$ = 85 kcal/mol,[19] we estimate[20] that $D[(CH_3)_3Si{-}CH_2CHCH_2] \simeq 71$ kcal/mol and that reaction 4a is exothermic by approximately 14 kcal/mol. The success of these displacement reactions, therefore, is a direct result of the substantial difference in Si–C and Si–F bond strengths.

Table I. Ionic Products of the Reactions of Fluoride Ion with Substituted Silanes

substituted silane, M	ionic products	approx % yield[a]
$(CH_3)_3SiCH_2CH{=}CH_2$	${}^-CH_2CH{=}CH_2$	96
	$(M - 1)^-$	4
$(CH_3)_3SiCH_2C_6H_5$	${}^-CH_2C_6H_5$	98
	$(M - 1)^-$	2
$(CH_3)_3SiC{\equiv}CC_2H_5$	${}^-C{\equiv}CC_2H_5$	91
	$(M - 1)^-$	9
$(CH_3)_3SiC{\equiv}C(n\text{-}C_4H_9)$	${}^-C{\equiv}C(n\text{-}C_4H_9)$	80
	$(M - 1)^-$	20
$(CH_3)_3SiC{\equiv}CCH_3$	${}^-C{\equiv}CCH_3$	92
	$(M - 1)^-$	8
$(CH_3)_3SiCH_2C{\equiv}CH$	${}^-CH_2C{\equiv}CH$	93
	$(M - 1)^-$	7
$(CH_3)_3Si$-(*cis*-$CH_2CH{=}CHCH_3$)	*cis*-${}^-CH_2CH{=}CHCH_3$	95
	$(M - 1)^-$	5
$(CH_3)_3Si$-(*trans*-$CH_2CH{=}CHCH_3$)	*trans*-${}^-CH_2CH{=}CHCH_3$	89
	$(M - 1)^-$	11
$(CH_3)_3SiC_6H_5$	$C_6H_5^-$	20
	$(M + F)^-$	65
	$(CH_3)_2(F)SiCH_2^-$	15
$(CH_3)_4Si$	$(M + F)^-$	94
	$(CH_3)_2(F)SiCH_2^-$	6
$(CH_3)_3SiCH{=}CH_2$	$(M + F)^-$	76
	$(CH_3)_2(F)SiCH_2^-$	24
$(CH_2{=}CH)_4Si$	$(M + F)^-$	100
$(CH_3O)_4Si$	$(M + F)^-$	100
$(CH_3)_3SiSi(CH_3)_3$	$(CH_3)_3Si^-$	100
$(CH_3)_2Si(CH_2CH{=}CH_2)$-$(CH_2C_6H_5)$	${}^-CH_2CH{=}CH_2$	27
	${}^-CH_2C_6H_5$	73

[a] Product distributions have not been corrected for mass discrimination and are intended to give a qualitative indication of the reaction branching ratio.

Similarly, fluoride ion reacts with benzyltrimethylsilane to generate the benzyl anion and with 1-(trimethylsilyl)-1-butyne and 1-(trimethylsilyl)-1-hexyne to generate the 1-butynyl and 1-hexynyl anions, respectively. In the latter case simple proton abstraction occurs in about 20% of the reactive encounters, reflecting the high acidity of hexyne. These reactions demonstrate that fluoride displacement of trimethylsilyl derivatives is a relatively clean and efficient mode for production of benzyl, alkenyl, and alkynyl anions.

To examine the specificity of formation of isomeric anions, we synthesized the 1- and 3-(trimethylsilyl)propynes. Both of these neutrals react readily with fluoride ion in the gas phase to generate $C_3H_3^-$ ions (eq 5 and 6). These anions exhibit different reactivity

$$F^- + (CH_3)_3SiC{\equiv}CCH_3 \rightarrow {}^-C{\equiv}CCH_3 + (CH_3)_3SiF \quad (5)$$

$$F^- + (CH_3)_3SiCH_2C{\equiv}CH \rightarrow {}^-CH_2C{\equiv}CH + (CH_3)_3SiF \quad (6)$$

toward a number of reagents, confirming their isomeric nature. For example, the propargyl anion reacts with molecular oxygen with a rate coefficient of $1 \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$; this is in excellent agreement with the value measured by Bohme and Young[17] for this reaction where $C_3H_3^-$ had been generated by proton abstraction from allene. The reaction of the methylacetylide anion with molecular oxygen proceeds with a rate coefficient 7 times smaller than that of the propargyl anion. The lower reactivity of the methylacetylide anion is consistent with the expectation that this species is the more stable isomeric form.

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(12) Smith, D.; Adams, N. G. *Gas Phase Ion Chem.* **1979**, *1*, 1–44.

(13) Slutsky, J.; Kwart, H. *J. Am. Chem. Soc.* **1973**, *95*, 8678–8685.

(14) Corey, E. J.; Kirst, H. A. *Tetrahedron Lett.* **1968**, *48*, 5041–5043.

(15) This value was calculated from $\Delta H_f°[(CH_3)_3SiF] = -126.0$ kcal/mol (Murphy, M. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 2085–5089), $\Delta H_f°[(CH_3)_3Si = +9$ kcal/mol (Davidson, I. M. T. *J. Organomet. Chem.* **1979**, *170*, 365–372), and $\Delta H_f°(F)$ = kcal/mol +18.9 (Stull, D. R.; Prophet, H. *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1971**, *NSRDS-NBS 37*).

(16) Franklin, J. L.; Harland, P. W. *Ann. Rev. Phys. Chem.* **1974**, *25*, 485–526.

(17) Bohme, D. K.; Young, L. B. *J. Am. Chem. Soc.* **1970**, *92*, 3301–3309.

(18) Zimmerman, A. H.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 3565–3568.

(19) Davidson, I. M. T. *J. Organomet. Chem.* **1979**, *170*, 365–372.

In separate experiments, we studied the reaction of molecular oxygen with $C_3H_3^-$ ions generated by proton abstraction from methylacetylene. The kinetics data indicate the presence of two species of different reactivity. These data confirm that proton abstraction from methylacetylene yields a mixture of isomers whereas fluoride ion displacement of the appropriate trimethylsilyl derivative generates a single species.

In an attempt to generate specific cis and trans isomers, we reacted fluoride ion with *cis*- and *trans*-1-(trimethylsilyl)-2-butene (eq 7 and 8). In both cases, $C_4H_7^-$ ions were cleanly and efficiently generated. However, we have not yet been able to demonstrate any difference in reactivity of these two species. There are several possible reasons for this. If the displacement reaction occurs through a long-lived intermediate, the integrity of the geometrical isomer may be lost by sequential processes similar to those represented in eq 2, i.e., resilylation within the initially formed complex. Alternatively the difference in stability of these species may be too small to probe by most chemical reactions. Or finally, upon interaction of the $C_4H_7^-$ ions with reacting neutrals, cis–trans isomerization of the ion may rapidly occur before reaction, thus obscuring their original isomeric nature. In any event, at the present time the method of fluoride displacement of substituted silanes cannot safely be used to generate cis–trans isomeric anions.

$$F^- + (CH_3)_3Si(\textit{cis}\text{-}CH_2CH{=}CHCH_3) \rightarrow \textit{cis}\text{-}^-CH_2CH{=}CHCH_3 + (CH_3)_3SiF \quad (7)$$

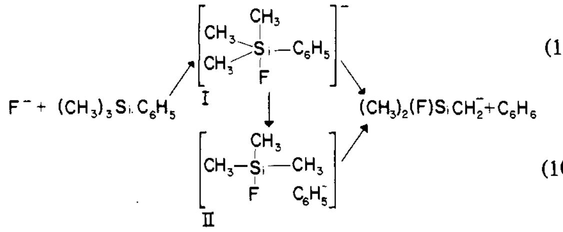
$$F^- + (CH_3)_3Si(\textit{trans}\text{-}CH_2CH{=}CHCH_3) \rightarrow \textit{trans}\text{-}^-CH_2CH{=}CHCH_3 + (CH_3)_3SiF \quad (8)$$

The reaction of fluoride with phenyltrimethylsilane is interesting as it exhibits new reaction pathways (eq 9). The phenyl anion is considerably more basic[3] than the ions discussed above, and its production by fluoride displacement of the silane represents only 20% of the reactive encounters. Since the phenyltrimethylsilane contains only relatively nonacidic hydrogen atoms, the proton abstracted product is present in only trace amounts. The major products correspond to addition (eq 9b) and to addition followed by loss of benzene (eq 9c). This latter product may arise by the following mechanism:

$$F^- + (CH_3)_3SiC_6H_5 \rightarrow C_6H_5^- + (CH_3)_3SiF \quad (9a)$$

$$\rightarrow (CH_3)_3(C_6H_5)SiF^- \quad (9b)$$

$$\rightarrow (CH_3)_2(F)SiCH_2^- + C_6H_6 \quad (9c)$$



(10a)

(10b)

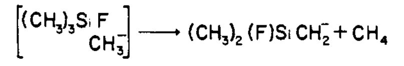
Addition generates a pentacoordinate silicon compound (I) which decomposes by cleavage of the Si–C and a C–H bond in a concerted four-center reaction. Alternatively, an intermediate complex (II) is formed in which fluorine has displaced the phenyl group; the phenide ion then abstracts a proton from the newly formed trimethylsilyl fluoride to generate the products. This second mechanism is appealing; as will be discussed below, we have demonstrated that the amide ion (which has similar basicity to the phenide ion)[3] is sufficiently basic to abstract a proton from tetramethylsilane.

We investigated the reactions of a number of other trimethylsilyl derivatives with fluoride ion to explore the possibility of forming new, highly reactive species such as methyl or vinyl anion. However, in the reactions of fluoride ion with tetramethylsilane and vinyltrimethylsilane, formation of the fluoride–silane adduct was the major product and $(CH_3)_2(F)SiCH_2^-$ was the minor product (eq 11). No methide or vinyl anions were observed. In contrast to the reaction of allyltrimethylsilane (eq 4a), the carbon–silicon bond in tetramethylsilane is stronger (85 kcal/mol)[19] and the electron affinity of the displaceable radical is smaller [EA(CH_3) = 1.8 kcal/mol][21] so that the net displacement reaction generating methide ion (eq 11c) is endothermic by about 9 kcal/mol. If the highly basic[3] CH_3^- species is formed during the reaction, it must quantitatively remove a proton before leaving the ion dipole complex (eq 12).

$$F^- + (CH_3)_4Si \rightarrow (CH_3)_4SiF^- \quad (11a)$$

$$\rightarrow (CH_3)_2(F)SiCH_2^- + CH_4 \quad (11b)$$

$$\not\rightarrow CH_3^- + (CH_3)_3SiF \quad (11c)$$



$$\left[(CH_3)_3Si\,F \atop CH_3^-\right] \longrightarrow (CH_3)_2(F)SiCH_2^- + CH_4 \quad (12)$$

For a number of silyl substrates the exclusive product is the pentacoordinate adduct; such adducts are especially favored by the presence of electronegative groups attached to silicon. Tetravinylsilane, for example, reacts with fluoride to form only the tetravinylfluorosilane anion (eq 13). Similarly the strongly basic cyclopropyl and benzoyl anions were not formed upon reaction of fluoride with cyclopropyl- or benzoyltrimethylsilane.

$$F^- + (CH_2{=}CH)_4Si \rightarrow (CH_2{=}CH)_4SiF^- \quad (13)$$

Reaction of fluoride ion with tetramethoxysilane does not generate methoxide ions (eq 14). The greater strength of the Si–O bond (108 kcal/mol)[22] as compared to the Si–C bond (70–85 kcal/mol) and the inductive stabilization of the pentacoordinate adduct probably account for this failure. Similarly, the reaction of fluoride with trimethylmethoxysilane is a poor source of methoxide ion. However a variety of other interesting anions can be generated in this way; for example, the trimethylsilyl anion results from attack of fluoride on hexamethyldisilane (eq 15).

$$F^- + (CH_3O)_4Si \not\rightarrow CH_3O^- + (CH_3O)_3SiF \quad (14a)$$

$$\rightarrow (CH_3O)_4SiF^- \quad (14b)$$

$$F^- + (CH_3)_3Si{-}Si(CH_3)_3 \rightarrow (CH_3)_3Si^- + (CH_3)_3SiF \quad (15)$$

One intriguing extension of this work involves the competitive displacement of two substituents:

$$F^- + (CH_3)_2Si(CH_2CH{=}CH_2)(CH_2C_6H_5) \rightarrow {}^-CH_2CH{=}CH_2 + (CH_3)_2(C_6H_5CH_2)SiF \quad (16a)$$

$$\rightarrow {}^-CH_2C_6H_5 + (CH_3)_2(CH_2{=}CHCH_2)SiF \quad (16b)$$

In this preliminary study we observed preferential displacement of the less basic benzyl anion; further experiments are in progress to explore the generality of this method for studying ion stabilities.

The reactions of amide, hydroxide, and methoxide with allyltrimethylsilane, tetramethylsilane, and vinyltrimethylsilane are summarized in Table II. All three anions are considerably more basic than fluoride; Bartmess and McIver[3] give the gas-phase acidities of their conjugate acids as 403 kcal/mol for NH_3, 391 kcal/mol for H_2O, 379 kcal/mol for CH_3OH, and 371 kcal/mol for HF. As a result, proton abstraction is an important pathway in the reactions of NH_2^-, OH^-, and CH_3O^- with trimethylsilanes which contain acidic hydrogens, for example

$$NH_2^- + (CH_3)_3SiCH_2CH{=}CH_2 \rightarrow (CH_3)_3Si\overset{-}{C}HCH{=}CH_2 + NH_3 \quad (17a)$$

$$\rightarrow {}^-CH_2CH{=}CH_2 + (CH_3)_3SiNH_2 \quad (17b)$$

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(20) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976; p 309.

(21) Ellison, G. B.; Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 2556–2558.

(22) Huheey, J. E. "Inorganic Chemistry: Principles of Structure and Reactivity"; Harper and Row: New York, 1972; p 699.

Table II. Ionic Products of the Reactions of Amide, Hydroxide, and Methoxide Ions with Substituted Silanes[a]

Neutral Reactant (M) = $(CH_3)_3SiCH_2CH{=}CH_2$

reactant ion	product ion				
	$^-CH_2CH{=}CH_2$	$(M-1)^-$	$(adduct)^-$	$(adduct - CH_4)^-$	$(adduct - C_3H_6)^-$
NH_2^-	+	+	–	–	–
OH^-	+	+	–	–	–
CH_3O^-	+	+	–	–	–

Neutral Reactant (M) = $(CH_3)_4Si$

reactant ion	product ion			
	CH_3^-	$(M-1)^-$	$(adduct)^-$	$(adduct - CH_4)^-$
NH_2^-	–	+	–	+
OH^-	–	–	–	+
CH_3O^-	–	–	+	trace

Neutral Reactant (M) = $(CH_3)_3SiCH{=}CH_2$

reactant ion	product ion				
	CH_2CH^-	$(M-1)^-$	$(adduct)^-$	$(adduct - CH_4)^-$	$(adduct - C_2H_4)^-$
NH_2^-	–	+	–	+	+
OH^-	–	trace	–	+	+
CH_3O^-	–	trace	+	–	+

[a] Symbols: (+) indicates that the ion was observed; (–) indicates that the ion was not observed; trace indicates that only a small amount of the ion was observed.

However the displacement reaction to form the allyl anion (eq 17b) is also observed for all three reactant ions.

With tetramethylsilane, which contains neither acidic nor displaceable groups, NH_2^-, OH^-, and CH_3O^- undergo different reactions. Amide, the most reactive anion of the three, is sufficiently basic to abstract a proton; the major product, however, corresponds to formation of an adduct with loss of methane (eq 18).

$$NH_2^- + (CH_3)_4Si \rightarrow (CH_3)_3SiCH_2^- + NH_3 \quad (18a)$$

$$\rightarrow (CH_3)_3SiNH^- + CH_4 \quad (18b)$$

The less basic hydroxide ion exhibits a single rapid pathway in which addition and loss of methane generates the trimethylsiloxide ion.

$$OH^- + (CH_3)_4Si \rightarrow (CH_3)_3SiO^- + CH_4 \quad (19)$$

Finally, the methoxide anion reacts with tetramethylsilane exclusively by addition (eq 20). Only a trace of methane elimination from the adduct is observed.

$$CH_3O^- + (CH_3)_4Si \rightarrow (CH_3)_4(CH_3O)Si^- \quad (20)$$

The reactions of vinyltrimethylsilane with amide, hydroxide, and methoxide are similar to their reactions with tetramethylsilane (eq 21) except there is now competition between loss of methane

$$NH_2^- + (CH_3)_3SiCH{=}CH_2 \rightarrow (CH_3)_2(CH_2{=}CH)SiCH_2^- + NH_3 \quad (21a)$$

$$\rightarrow (CH_3)_3SiNH^- + C_2H_4 \quad (21b)$$

$$\rightarrow (CH_3)_2(CH_2{=}CH)SiNH^- + CH_4 \quad (21c)$$

and ethylene from the silane–anion adduct. Again amide is sufficiently basic to effect proton abstraction. The major product corresponds to addition of amide with loss of ethylene (eq 21b) while addition with loss of methane is also evident (eq 21c).

The reactions of hydroxide (eq 22) are similar except that the

$$OH^- + (CH_3)_3SiCH{=}CH_2 \rightarrow (CH_3)_3SiO^- + C_2H_4 \quad (22a)$$

$$\rightarrow (CH_3)_2(CH_2{=}CH)SiO^- + CH_4 \quad (22b)$$

proton abstraction pathway is absent. Finally methoxide reacts primarily by addition (eq 23); the anion corresponding to loss of

$$CH_3O^- + (CH_3)_3SiCH{=}CH_2 \rightarrow (CH_3)_3(CH_2{=}CH)(CH_3O)Si^- \quad (23a)$$

$$\rightarrow (CH_3)_2(CH_3O)SiCH_2^- + C_2H_4 \quad (23b)$$

ethylene from the adduct is observed, whereas the anion corresponding to loss of methane is not.

Conclusion

In summary, the reactions of fluoride, amide, hydroxide, and methoxide ions with substituted silanes proceed by a variety of interesting pathways. Fluoride ion reacts primarily by displacement to generate anions less basic than phenide; small amounts of proton abstraction from the silanes also occur. Specific generation of structural isomers by this method has been demonstrated; cis–trans isomeric silanes have also been reacted, but it was not possible to confirm the isomeric identity of the anions produced. When the substituted silanes do not contain a displaceable group, the fluoride ion reactions generate simple adducts and adducts which have eliminated benzene, methane, or ethylene. Alkoxide ions were not generated by fluoride displacement reactions presumably because of the strong silicon–oxygen bond in the substituted silane. Competitive displacement reactions offer a promising method for probing relative ion stabilities.

Due to their greater basicity, amide, hydroxide, and methoxide react with silanes containing displaceable groups (e.g., allyltrimethylsilane) by both proton abstraction and displacement. With silanes not containing displaceable groups (e.g., tetramethylsilane and vinyltrimethylsilane) completely different mechanisms are operable. Products corresponding to addition with loss of methane or, preferentially, loss of ethylene were observed. Amide also induces proton abstraction, and methoxide also exhibits simple addition.

In conclusion, these results demonstrate an efficient method of producing specific isomeric anions in the absence of acidic neutral precursors, they illustrate some mechanistically interesting chemistry, and they offer a variety of intriguing prospects for further research.

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