

ACCOUNTS OF CHEMICAL RESEARCH

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Gas-Phase Negative Ion Chemistry of Organosilanes

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Organosilicon compounds are playing an increasingly important role in synthetic organic chemistry, and the chemistry of their anions is the subject of a great deal of current interest.¹ Organosilicon anion chemistry is potentially even richer than that of carbanion chemistry since silyl anions, α -silyl carbanions, pentacoordinate silicon anions, and hexacoordinate silicon anions are useful synthetic reagents. In addition, pentacoordinate silicon anions play key roles as reaction intermediates

Charles H. DePuy was born in Detroit, MI, and received his undergraduate education at Berkeley. His Ph.D. (1953), under the direction of William Doering, was begun at Columbia University and completed at Yale. After a year's postdoctoral work with Donald Cram at UCLA, he joined the faculty of Iowa State University and in 1963 moved to his present position at Colorado. After many years of studying organic reaction mechanisms in solution, he "entered the gas phase", and his present research is entirely devoted to this area of chemistry.

Robert Damrauer was born in Toledo, OH, and received his undergraduate degree at the University of Michigan. Working under Dietmar Seyferth's tutelage, he received his Ph.D. at the Massachusetts Institute of Technology. After a year of postdoctoral work at Harvard with P. D. Bartlett, he joined the faculty at the University of Colorado at Denver, where he remains ensconced.

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and in favorable cases are stable species.

However, in part because of the myriad of reactions which organosilicon compounds can undergo in the presence of strong bases, the negative ion chemistry of organosilicon compounds can be even more difficult to study in solution than that of carbanions because added to the problems of ion pairing and aggregation are those of isomerism and polymerization. We, therefore, became attracted to the study of the gas-phase negative ion chemistry of organosilanes in the hope that the study of some of these anions in the absence of solvent and counterions could make a contribution to our understanding of these important species.² Two quite different gas-phase techniques have been used in these studies. We have individually written reviews on ion cyclotron resonance spectroscopy (ICR)³ and flowing afterglow (FA)⁴ and will not repeat experimental details here. Nevertheless, for readers unacquainted with the field of gas-phase ion-molecule reactions, a few words

(1) (a) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: New York, 1983. (b) Colvin, E. *Silicon in Organic Synthesis*; Butterworths: Boston, MA, 1981. (c) Fleming, I. In *Comprehensive Organic Chemistry*; Pergamon: Oxford, 1979; Chapter 13. (d) Magnus, P. D.; Sarkar, T.; Djuric, S. *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, 1982; Chapter 48.

(2) For a recent review of gas-phase ion chemistry of silicon compounds with an emphasis on positive ions, see: Oppenstein, A.; Lampe, F. W. *Rev. Chem. Intermed.* **1986**, *6*, 275.

(3) Bowie, J. H. *Acc. Chem. Res.* **1980**, *13*, 76.

(4) (a) DePuy, C. H.; Bierbaum, V. M. *Acc. Chem. Res.* **1981**, *14*, 146. (b) DePuy, C. H.; Grabowski, J. J.; Bierbaum, V. M. *Science* **1982**, *218*, 955.

of background are necessary.

Gas-phase ion-molecule reactions can occur very rapidly, with bimolecular rate constants as high as 10^{12} L molecule⁻¹ s⁻¹ (2×10^{-9} cm³ molecule⁻¹ s⁻¹), because ions attract neutral reagents by ion-dipole and ion-induced dipole forces (which can amount to 10–20 kcal mol⁻¹ relative kinetic energy by the time the species are within reaction distance).⁵ The ion and the neutral enter into a relatively long lived (typically 10^{-7} to 10^{-12} s) complex in which part or all of this energy can be used to surmount reaction barriers. Unless the complex lives long enough to dissipate its internal energy by collision with a third body, it dissociates, either back to reactants or on to two or more products; adducts between the ion and neutral are uncommon but are more often seen at the higher pressures (≈ 0.5 Torr) of the FA than at the lower pressures ($\approx 10^{-5}$ Torr) of the ICR experiments. In discussing reactivities in the gas phase, it is best to compare "reaction efficiencies" (reactions per ion-molecule encounter) rather than reaction rates themselves, since an ion will collide much more often with a polarizable molecule with a dipole moment, like H₂O, than it will with, for example, H₂ which has no dipole moment and is only weakly polarizable. Encounter rates (also called collision or capture rates) can be calculated with reasonable precision.

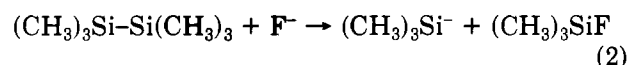
One can seldom generate a specific organic anion of interest directly. Instead, highly reactive inorganic anions or organic bases are produced by electron impact on appropriate precursors, and these in turn are used to produce organic anions by proton transfer or other chemical reactions. In the FA, hydroxide ion is formed from N₂O and CH₄, amide ion from ammonia, and fluoride ion from NF₃. In the ICR methoxide ion is a frequent initial ion, arising from electron impact on methyl nitrite. Amide, hydroxide, and methoxide ions are all extremely strong bases in the gas phase, capable of extracting a proton from most organic molecules.⁶ Fluoride ion is also a relatively strong base but is used primarily because of its great affinity for silicon.⁷

It must not be thought that because ion-molecule processes are so fast, they are necessarily unselective in their reactions. On the contrary, many are highly discriminating; large hydrogen-deuterium isotope effects have been observed in, for example, base-induced E2 reactions in the gas phase.⁸ Indeed, in the vast majority of reactions, there is an excellent correspondence between the products and mechanisms observed from a given gas-phase anion-molecule reaction and from the same reaction in solution. We therefore feel confident that the results of our studies on the chemistry of various anions from silanes in the gas phase can be applied as models for these same reactions in solution.

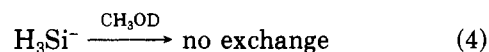
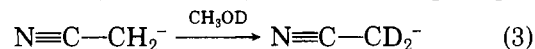
Formation and Basicity of R₃Si⁻ and R₃SiCH₂⁻

The silyl anion, SiH₃⁻, can readily be prepared by proton abstraction from SiH₄ with amide ion or other

strong bases, and the acidity of SiH₄ has been determined in an ICR to be 371 ± 2 kcal mol⁻¹.⁶ Silane is thus found to be about as strong an acid as acetonitrile, HF, *tert*-butyl alcohol, and dimethyl sulfoxide and to be significantly more acidic than water, propylene, or toluene. Tetramethylsilane is much less acidic than SiH₄, falling in acidity near water (391 kcal mol⁻¹), a region in which accurate acidity standards are lacking. Surprisingly though, proton abstraction from methylsilanes gives rise mainly or exclusively to α -silyl carbanions. When trimethyldeuteriosilane was allowed to react with methoxide ion in the ICR, a small amount of proton, but no deuterium, abstraction was observed.⁹ In the FA large amounts of the M - 1 anion result from reaction of trimethylsilane with NH₂⁻. Chemical reactions (vide infra) clearly show this to be the α -silyl carbanion (eq 1).¹⁰ An authentic trimethylsilyl anion arises from reaction of hexamethyldisilane with fluoride ion (eq 2).¹¹



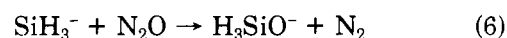
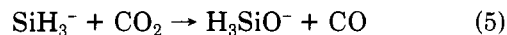
The slowness with which protons are transferred to and from silicon as compared to those attached to carbon in the gas phase manifests itself in yet another way. Hydrogen-deuterium exchange reactions are commonly observed in the gas phase when a carbanion containing hydrogens is allowed to react with D₂O or a deuterated alcohol.¹² For example, the anion from acetonitrile readily exchanges two hydrogens for deuterium in the presence of CH₃OD, *t*-BuOD, or D₂O (eq 3). Silyl anions, in contrast, do not exchange (eq 4)



although, by virtue of their basicity relative to that of methoxide ion, they would be expected to do so readily. In this respect, there is a sharp contrast between first- and second-row elements, one which carries over to the chemistry of -S-H and -P-H compounds.¹¹

Reactions of R₃Si⁻ and R₃SiCH₂⁻

The chemistry of silyl anions and α -silyl carbanions is dominated in the gas phase, as it is in solution, by the tendency of silicon to form strong bonds to oxygen, nitrogen, and sulfur. Thus, SiH₃⁻ reacts with CO₂, N₂O, and CS₂ by oxygen or sulfur transfer:¹³



Although these reactions appear superficially similar, we believe that they occur by fundamentally different mechanisms. This belief is based partly upon analogy with other gas-phase ion processes and is supported by high-level ab initio molecular orbital calculations of the

(9) Klass, G.; Trenerry, V. C.; Sheldon, J. C.; Bowie, J. H. *Aust. J. Chem.* 1981, 34, 519.

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

(11) Kass, S. R.; DePuy, C. H.; Damrauer, R., unpublished results.

(12) (a) Stewart, J. H.; Shapiro, R. H.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* 1977, 99, 7650. (b) DePuy, C. H.; Bierbaum, V. M.; King, G. K.; Shapiro, R. H. *J. Am. Chem. Soc.* 1978, 100, 2921.

(13) Sheldon, J. C.; Bowie, J. H.; DePuy, C. H.; Damrauer, R. *J. Am. Chem. Soc.* 1986, 108, 6794.

(5) Various aspects of gas-phase ion chemistry are surveyed in: *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979, 1984; Vol. 1-3.

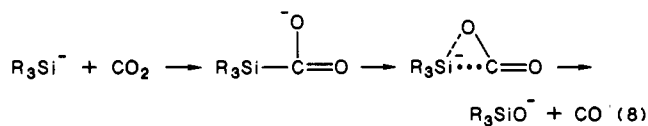
(6) Bartmess, J. E., to be submitted for publication in *J. Phys. Chem. Ref. Data*. Also see Chapter 11, Vol. 2, of ref 5.

(7) Walsh, R. *Acc. Chem. Res.* 1981, 14, 246.

(8) Bierbaum, V. M.; Filley, J.; DePuy, C. H.; Jarrold, M. F.; Bowers, M. T. *J. Am. Chem. Soc.* 1985, 107, 2818.

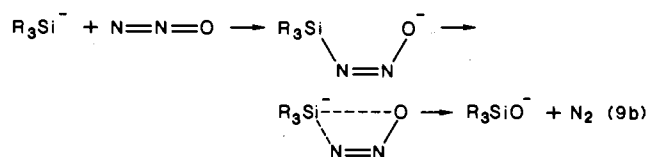
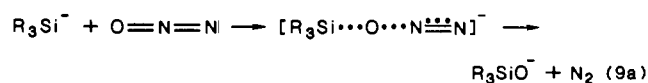
energy surfaces for these reactions.

Reaction of SiH_3^- (and other silyl anions) with CO_2 is rapid ($k = 6.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, reaction efficiency 0.60), and the siloxide is the only product. We suggest that addition to form the carboxylate occurs first as it does in solution^{1b} (an analogous product is observed from reaction of allyl anion with CO_2 for example¹⁴) but is followed by rearrangement through a transition state involving a pentacoordinate silyl anion (eq 8). Calculations¹³ (6-311++G) of the energy surface



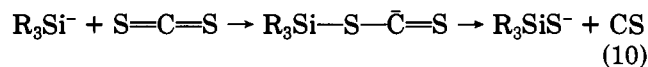
for this reaction fail to reveal a low-energy pathway for direct attack on oxygen (with subsequent or simultaneous loss of CO) but do suggest that rearrangement from an initial adduct can occur via oxygen addition to silicon.

Reaction of R_3Si^- with N_2O is much slower; only 1 in 1000 collisions of SiH_3^- with N_2O results in reaction. Two extreme mechanisms can be written:¹³



Direct attack on oxygen, as in (9a), is of course attractive since a nitrogen molecule could then be formed in the transition state of the reaction, and the great overall exothermicity of the reaction could manifest itself in the rate-determining step. In spite of this apparent advantage for (9a), we favor the mechanism illustrated in eq 9b, in which attack occurs on nitrogen with subsequent oxygen atom transfer via a four-membered ring. Ab initio calculations support this stepwise pathway. In addition, we have studied the reactions of numerous anions with N_2O and found in each case that reaction occurs via initial attack at nitrogen rather than oxygen.¹⁵

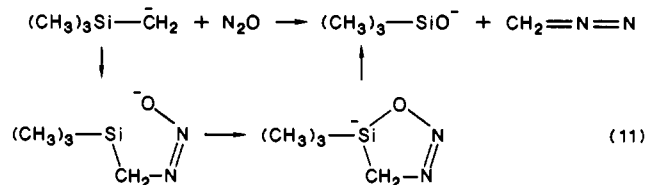
When silyl anions react with CS_2 (and COS), we favor a mechanism involving direct attack on sulfur with expulsion of CS (or CO):



Such a path is strongly supported by ab initio calculations, in sharp contrast with the results calculated for the CO_2 reaction.¹³ We have frequently seen sulfur transfer from COS and CS_2 to carbanions and even to NH_2^- and OH^- ,^{15b} whereas we have never seen oxygen transfer to these species from CO_2 . Quite likely the ability of sulfur to stabilize an intermediate anion plays an important role in allowing this mechanism to operate.

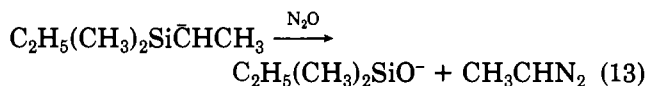
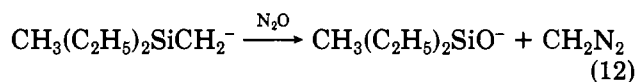
Silyl anions also undergo oxygen atom transfer reactions to form siloxides when allowed to react with SO_2 and cyanates (RNCO). They also react as a nucleophile in $\text{S}_\text{N}2$ displacement reactions. The trimethylsilyl anion, for example, reacts with methyl chloride to form Cl^- with a rate constant of $1.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (reaction efficiency 0.1).¹⁶ For comparison, the allyl anion reacts about 2 times^{17a} and HO^- about 10 times^{17b} more rapidly with this same reagent.

α -Silyl carbanions also form siloxides when allowed to react with N_2O , but the overall reaction involves the loss of the side chain as shown in eq 11. This reaction

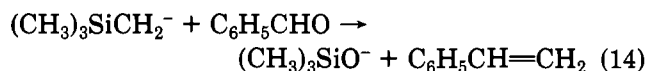


is a useful one for distinguishing isomeric silyl and α -silyl carbanions, since silyl anions form siloxides by adding an oxygen atom (formation of an M + 16 anion) while the α -silyl carbanions replace, for example, a CH_2 group by oxygen (formation of an M + 2 anion).

Reaction with N_2O is also useful for determining the site of deprotonation in unsymmetrically substituted silanes. Proton abstraction from dimethyldiethylsilane can occur from either the methyl or ethyl group, producing a mixture of ions of identical masses. The composition of the mixture can be determined by allowing it to react with N_2O ; from one ion an O^- replaces a CH_2^- group (eq 12), and from the other it replaces a C_2H_4^- (eq 13).

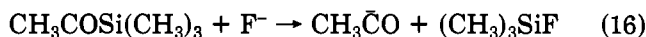


α -Silyl carbanions also undergo the gas-phase Peterson reaction when allowed to react with carbonyl compounds, especially those which do not have acidic protons (eq 14).¹⁶



Pentacoordinate Silicon Anions as Intermediates and Products

Pentacoordinate silicon anions play key roles as reaction intermediates in the gas phase as they do in solution. For example, appropriately substituted silanes are extremely useful substrates for the generation of specific anions in the gas phase, anions which might not arise by proton abstraction from the corresponding neutral (eq 15 and 16).^{9,18-20} These reactions are un-



(16) Damrauer, R.; DePuy, C. H., unpublished results.

(17) (a) McDonald, R. N.; Chowdhury, A. C. *J. Am. Chem. Soc.* **1982**, *104*, 901. (b) Bohme, D. K.; MacKay, G. I.; Payzant, J. D. *J. Am. Chem. Soc.* **1974**, *96*, 4027.

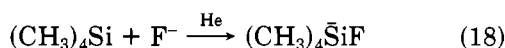
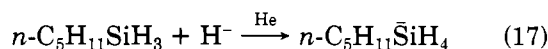
(18) DePuy, C. H.; Bierbaum, V. M.; Flippin, L. A.; Grabowski, J. J.; King, G. K.; Schmitt, R. J.; Sullivan, S. A. *J. Am. Chem. Soc.* **1979**, *101*, 6443.

(14) Bierbaum, V. M.; DePuy, C. H.; Shapiro, R. H. *J. Am. Chem. Soc.* **1977**, *99*, 5800.

(15) (a) Kaas, S. R.; Filley, J.; Van Doren, J. M.; DePuy, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 2849. (b) Bierbaum, V. M.; Grabowski, J. J.; DePuy, C. H. *J. Phys. Chem.* **1984**, *88*, 1389.

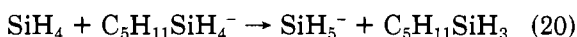
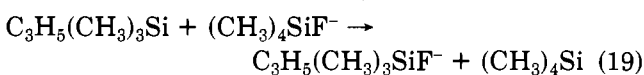
doubtedly facilitated by the ease with which the nucleophile adds to silicon and the ability of silicon to be pentacoordinate. This is particularly apparent in the case of F^- because of the strength of the silicon-fluorine bond. In contrast to the situation in solution, however, pentacoordinate silicon species can readily be detected in the gas phase and their properties and subsequent reactions studied.

An adduct will only form in a gas-phase collision between a neutral reagent and an anion if the collision complex lives long enough to transfer its excess energy to the buffer gas. In a FA at 0.5 Torr for example, only 1 in 250 collisions between HO^- and CO_2 results in the formation of HCO_3^- ,²¹ and no adducts are observed by reaction of H^- or F^- with SiH_4 .²² However, the attachment of one or more alkyl groups to the silicon atom in place of hydrogen greatly increases the efficiency of both of these latter reactions (eq 17 and 18).



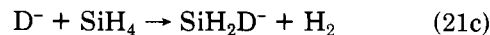
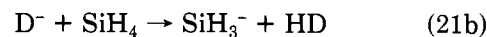
Presumably, the reaction exothermicity can be dispersed into vibrations and rotations of the alkyl group(s), extending the lifetime of the complex sufficiently to allow collisions with the buffer gas. Tetramethylsilane, for example, gives a stable adduct with F^- at every collision in the FA.¹⁶

Once a pentacoordinate silyl anion has been formed and cooled by the buffer gas, its fluoride ligand can be transferred to another molecule in a reaction which is much less exothermic than that involving fluoride ion itself. For example, when allyltrimethylsilane reacts with F^- , allyl anion results. When it reacts with tetramethylfluorosilane anion, the allyltrimethylfluorosilane anion is formed instead by fluoride ion transfer (eq 19). Similarly, the parent SiH_5^- arises by hydride ion transfer from the stabilized hydride adduct (eq 20).²²

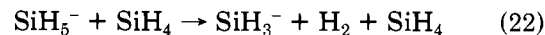


Recent theoretical^{23,24} and experimental^{22,25} studies have converged on the reactions of silanes with hydride ions. Ab initio calculations (6-21G level) show that H^- should react at the silicon atom of silane without a barrier to form SiH_5^- and at the hydrogen atom to form SiH_3^- and H_2 . Calculations using diffuse functions (6-31⁺⁺G) reveal a small barrier of 6 kcal mol⁻¹ for proton abstraction. Both SiH_5^- and $SiH_3^- \cdots H_2$ are predicted to be stable, i.e., to exist in potential wells, but since they are formed in exothermic reactions, the overall reaction to form SiH_3^- and H_2 is the only one expected to be observed.²³ Bohme²⁵ has shown that hydride reacts with SiH_4 to form SiH_3^- exclusively, although when D^- is used as the reactant ion, H^- and SiH_2D^- are also

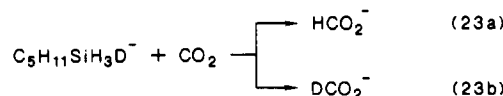
formed. Indeed, the rate at which H^- is formed exceeds that for formation of SiH_3^- or SiH_2D^- by at least a factor of 4 (eq 21a-21c). In agreement with the theoretical



predictions, SiH_5^- is a stable species, and a potent hydride donor, with the hydride affinity of SiH_4 estimated to fall within the range of 18-27 kcal mol⁻¹.²² It is, however, metastable with respect to SiH_3^- and H_2 , as the following reaction demonstrates:

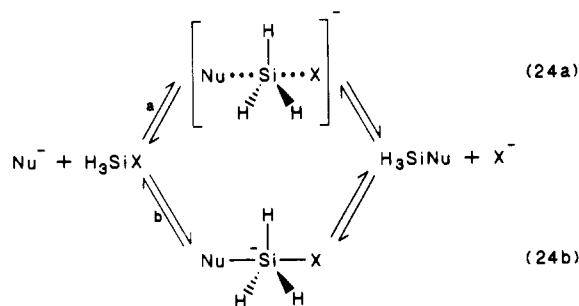


Squires²² has also shown that the hydrogens and deuterium attached to silicon in $C_5H_{11}SiH_3D^-$ become equivalent, and either may be transferred to CO_2 (eq 23); a deuterium isotope effect was found for the hydride transfer.



Nucleophilic Displacement Reactions on Silicon

There is ample evidence that gas-phase S_N2 reactions on carbon proceed by a mechanism completely analogous to that observed in solution, namely, by attack of the nucleophile at the rear and inversion of configuration by way of a five-coordinate transition state.²⁶ The rates of such reactions are dependent upon entropy (density of states) and enthalpy differences between reactants and transition states and have been extensively discussed in the literature. A silicon halide, R_3SiX , might in principle react through a single transition state as does carbon (eq 24a) or by way of a pentacoordinate silicon anion intermediate which decomposes to products (eq 24b):



Ab initio and MNDO calculations indicate that reaction by way of path 24a is not favored,^{23,27} even when the five groups around silicon are large; instead, a pentacoordinate intermediate is formed.^{23,28}

In order to compare gas-phase nucleophilic reactions at carbon and silicon, the rates of reaction of various anions with methyl iodide and trimethylchlorosilane were measured under FA conditions.²⁹ The results are

(19) DePuy, C. H.; Bierbaum, V. M.; Damrauer, R.; Soderquist, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 3385.

(20) Sheldon, J. C.; Bowie, J. H.; Hayes, R. N. *Nouv. J. Chim.* **1984**, *8*, 79.

(21) Fehsenfeld, F. C.; Ferguson, E. E. *J. Chem. Phys.* **1974**, *61*, 3181.

(22) Hajdasz, D. J.; Squires, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 3139.

(23) Sheldon, J. C.; Hayes, R. N.; Bowie, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 7711.

(24) See ref 22 for other theoretical calculations.

(25) Payzant, J. D.; Tanaka, K.; Betowski, L. D.; Bohme, D. K. *J. Am. Chem. Soc.* **1976**, *98*, 894.

(26) Olmsted, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219.

(27) Dewar, M. J. S.; Healy, E. *Organometallics* **1982**, *1*, 1705.

(28) The intermediacy of pentacoordinate silicon anions raises both the question of the geometry of such species and their interconversion. Although we have assumed trigonal-bipyramidal geometry and rapid interconversion of equatorial and axial positions, there is, at present, no specific experimental information bearing on such questions in the gas phase.

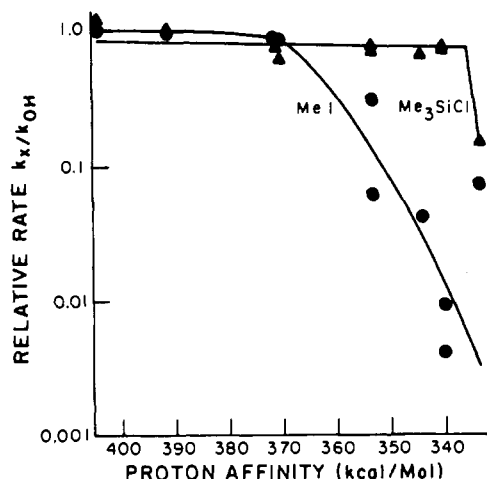
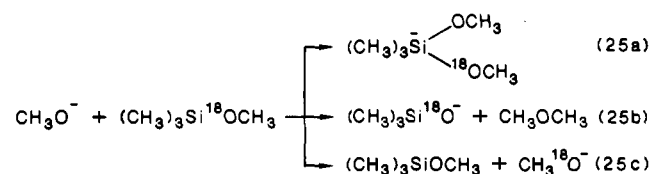


Figure 1.

dramatically different and are shown in Figure 1. For methyl iodide there is a gradual reduction in rate as the attacking nucleophile becomes less basic. In marked contrast, trimethylchlorosilane reacts at virtually every collision for exothermic reactions or not at all for endothermic ones. This is precisely the expected behavior if the pentacoordinate intermediate is formed at each collision. It is also consistent with studies on silicon displacement reactions in solution where stereochemical results are best accommodated by a mechanism involving the interconversion of substituents in a pentacoordinate intermediate.

Alkoxysilanes, R_3SiOR' , in contrast to dialkyl ethers, also undergo nucleophilic displacement reactions readily in the gas phase.⁹ The products are somewhat different, depending upon whether reaction is with an alkoxide (e.g., CH_3O^-) or with an alkoxide-alcohol cluster ion (e.g., $CH_3O^- \cdot HOCH_3$). When methoxide ion is used as the base in the FA, adduct formation is rapid (eq 25a). At lower pressures in the ICR, and to a small extent in the FA, S_N2 reaction (eq 25b) and ether exchange (eq 25c) can occur. When ethyl and larger alkylsilyl ethers

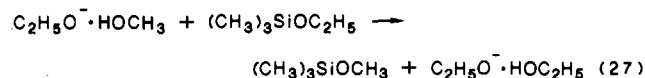
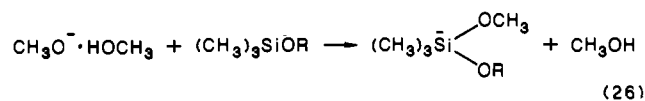


are allowed to react with methoxide ion, an $E2$ reaction also occurs. Ether interchange increases as the alkyl group becomes larger since larger alkoxide ions are weaker bases than methoxide, and the exchange reaction becomes exothermic.

When alkoxide-alcohol clusters are used as reactants,³⁰ only adduct formation and ether interchange are observed, even in the ICR. Adduct formation now becomes fast even at low pressures since the reaction exothermicity can be removed by the expulsion of an alcohol molecule (eq 26). When mixed clusters are used as reactant ions, an alkoxide exchange reaction is revealed (eq 27) (reaction efficiency 0.3). The surprising aspect of this reaction is its specificity; the smaller al-

(29) Damrauer, R.; DePuy, C. H.; Bierbaum, V. M. *Organometallics* 1982, 1, 1553.

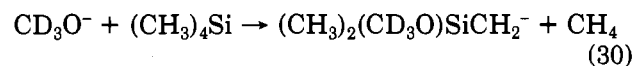
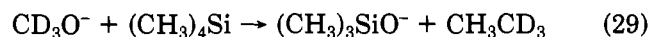
(30) Hayes, R. N.; Bowie, J. H.; Klass, G. *J. Chem. Soc., Perkin Trans. 2* 1984, 1167.



koxide ion (in this case CH_3O^-) reacts at silicon while the larger alcohol (C_2H_5OH) becomes part of the solvated ion. Similar reactions occur between alcohol cluster ions and carbon ethers,³¹ alkoxyboranes,³² and titanium alkoxides.³³ A preliminary ab initio study indicates that the specificity shown in eq 27 may be due to an initial orientation effect: $C_2H_5O^-$ hydrogen bonds to the ethoxy group of the silane, thus directing methanol toward silicon.³³

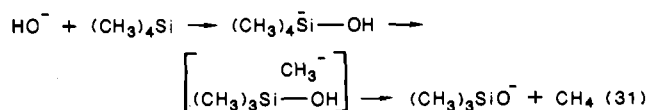
Alkane Eliminations from Pentacoordinate Silicon

We have described above how a pentacoordinate silicon anion is formed with excess energy. Unless this energy is removed, the ion will decompose. If it contains a reasonably good leaving group (allyl, alkoxide), the corresponding anion will be formed. If a reasonable leaving group is not present, decomposition by loss of an alkane is often observed. Three examples are



These reactions are of interest in themselves, but they are also useful as tools for gaining insights into properties of some simple anions.

So far, the reaction of HO^- with silanes has been the most extensively investigated of these cleavages.^{34,35} We picture the reaction as occurring analogously to that for the reaction of F^- with silanes, namely, by addition of the anion to form a pentacoordinate intermediate which then breaks down with expulsion, or attempted expulsion, of a carbanion. Indeed, if HO^- is allowed to react with allyltrimethylsilane, allyl anion is a major product, just as it is the exclusive product of fluoride ion reaction. However, when HO^- reacts with tetramethylsilane, the initially formed complex contains insufficient energy to generate the highly basic CH_3^- ion as a free species. We suggest, however, that CH_3^- begins to depart from the intermediate but immediately reacts with the proton from the attacking base (eq 31). In



agreement, if DO^- is used as the base, no deuterium is observed in the resulting siloxide ion.¹⁶ It was also found that when HO^- reacts with $(\text{CH}_3)_2(\text{CD}_3)_2\text{Si}$, the

(31) Hayes, R. N.; Paltridge, R. L.; Bowie, J. H. *J. Chem. Soc., Perkin Trans. 2* 1985, 567.

(32) Hayes, R. N.; Sheldon, J. C.; Bowie, J. H. *Organometallics* 1986, 5, 162.

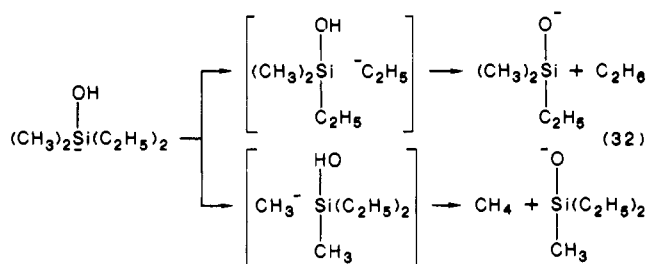
(33) Sheldon, J. C.; Hayes, R. N.; Bowie, J. H., unpublished observations.

(34) DePuy, C. H.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* 1984, 106, 4051.

(35) Sheldon, J. C.; Hayes, R. N.; Bowie, J. H.; DePuy, C. H. *J. Chem. Soc., Perkin Trans. 2*, in press.

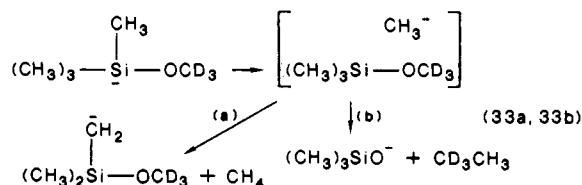
product ions $(\text{CH}_3)_2(\text{CD}_3)\text{SiO}^-$ and $\text{CH}_3(\text{CD}_3)_2\text{SiO}^-$ are formed in equal abundance.³⁵

We have used silane cleavage reactions by HO^- to gain an insight into the relative acidity of the simple hydrocarbons. While the acidity of methane can be calculated from its known bond dissociation energy and the electron affinity of the methyl radical, the acidities of ethane, propane, and other hydrocarbons less acidic than NH_3 are completely unknown. If incipient carbanions are intermediates in the cleavage reaction of silanes with HO^- , we might estimate the relative basicity of the alkyl anions (and hence the acidity of the alkanes) by measuring the relative loss of the two alkanes in unsymmetrical silanes. For example, when dimethyldiethylsilane is allowed to react with HO^- , nearly twice as much methane is lost as ethane (eq 32). This



suggests that the methyl anion is easier to expel and is therefore a *weaker* base than the ethyl anion.^{36,37} To calibrate the method, we compared the loss of methane to the loss of other molecules (H_2 , C_6H_6 , $\text{CH}_2=\text{CH}_2$, etc.) whose acidities are at least approximately known and found reasonable agreement with expectations.³⁴

Reactions 29 and 30 are thought to proceed analogously, but since the attacking base has no acidic protons, the methide ion must find other reaction pathways. It does so by proton abstraction from a methyl group (eq 33a) or by inducing an $\text{S}_{\text{N}}2$ displacement reaction on the methoxyl group (eq 33b).^{9,35} This latter



process must involve an extensive movement of the methyl anion from silicon to the rear of the CD_3 group. *Ab initio* calculations (3-21 G) for this type of reaction are shown in Figure 2 for the model system $\text{CH}_3\text{O}^-/\text{CH}_3\text{SiH}_3$. Interestingly, such reactions show secondary deuterium isotope effects. For example, reaction of CD_3O^- with $(\text{CH}_3)_2(\text{CD}_3)_2\text{Si}$ in the ICR gives product ions $\text{CH}_3(\text{CD}_3)_2\text{SiO}^-$ and $\text{CD}_3(\text{CH}_3)_2\text{SiO}^-$ in the ratio 6:4 ($\text{H}/\text{D} = 1.5$). This is consistent with a high barrier (cf. Figure 2). In contrast, reaction 28 has a smaller barrier and shows no isotope effect.³⁵

Other Silicon-Containing Anions

There has been much recent interest in compounds containing multiple bonds to silicon ($\text{Si}=\text{O}$, $\text{Si}=\text{C}$). Neutral molecules of these types have been generated and studied in detail in the gas phase.³⁸ Such species

(36) Spitznagel, G. W.; Clark, T.; Chandrasekhar, J.; Schleyer, P. v. *R. J. Comput. Chem.* 1982, 3, 363.

(37) An alternative mechanistic view is presented in: Tumas, W.; Foster, R. F.; Brauman, J. I. *J. Am. Chem. Soc.* 1984, 106, 4053.

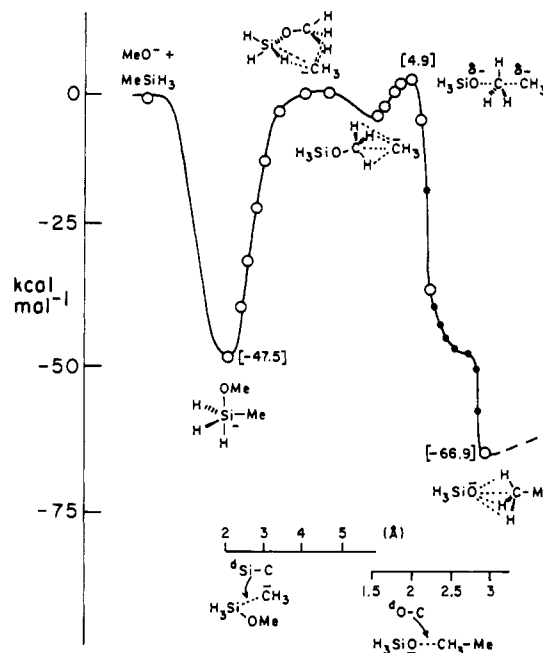
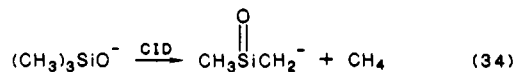


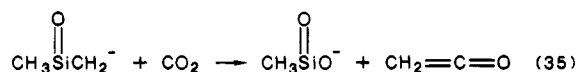
Figure 2.

are usually highly reactive, and as a result their chemistry is complex and often difficult to study. This seems to be an area in which gas-phase ion-molecule studies could play an especially vital role. Thus, anions containing multiply bonded silicon atoms could be prepared and their reactions compared with those of their carbon analogues. Another approach would be to generate the neutral unsaturated molecules in the dilute phase and to examine their reactions with anions of various types. Both approaches have recently been carried out successfully.

Squires has prepared a silaenolate ion in the gas phase and studied some of its chemical reactions.³⁹ Silaacetone enolate was formed by collisionally induced decomposition (CID) of Me_3SiO^- (eq 34). One inter-



esting reaction of the silaenolate is with CO_2 to form the silaacetate ion (eq 35). These approaches promise



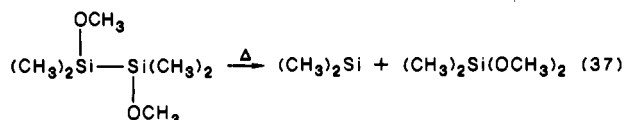
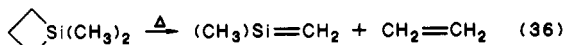
to provide ways of making a number of new and unusual silicon-containing anions. Brauman has also recently reported the formation of the silaacetate enolate ion.⁴⁰ This ion forms by photodissociation of Me_3SiO^- ; in contrast, vibrationally induced electron detachment gives the trimethylsiloxide radical.

We have recently equipped a flowing afterglow with a pyrolyzer so that highly reactive neutrals can be added to the flow tube. Both dimethylsilene (eq 36) and dimethylsilylene (eq 37) have been generated and allowed

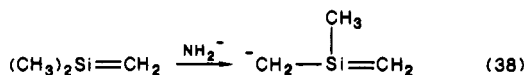
(38) (a) Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* 1979, 79, 529. (b) Bertrand, G.; Trinquier, G.; Mazerolles, P. *J. Organomet. Chem. Libr.* 1981, 12, 1. (c) West, R. *Pure Appl. Chem.* 1984, 56, 163. (d) Gaspar, P. P. In *Reactive Intermediates*; Wiley: New York, 1980-1982; Vol. 1, 2. (e) Raabe, G.; Michl, J. *Chem. Rev.* 1985, 85, 419.

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

(40) Tumas, W.; Salomon, K. E.; Brauman, J. I. *J. Am. Chem. Soc.* 1986, 108, 2541.



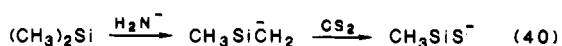
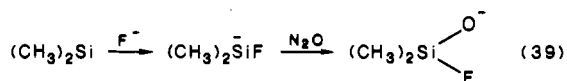
to react with anions.^{41,42} Dimethylsilene, $\text{Me}_2\text{Si}=\text{CH}_2$, can be detected in the FA by reaction with F^- and either H_2N^- or HO^- , the first giving an anion resulting from fluoride addition at silicon and the second, the $M-1$ anion obtained from proton abstraction from carbon. Our efforts have concentrated on the chemistry of the $M-1$ anion obtained from proton abstraction (eq 38).



The silaallyl ion formed was characterized by its reactions with CO_2 , CS_2 , and COS . This ion and its carbon analogue, the $M-1$ anion of isobutene, have quite different reactivities. For example, the carbon analogue reacts with N_2O giving a diazo anion¹⁴ while the silicon species does not react at all with this reagent.

The acidity of dimethylsilene was measured by standard acid-base studies. Comparison of its acidity (approximately $377 \text{ kcal mol}^{-1}$) with that of isobutene ($390 \text{ kcal mol}^{-1}$) indicates a substantial stabilizing effect by silicon, greater than that in $\text{MeSi}(\text{=O})\text{CH}_2^-$ ³⁹ but less than in $\text{Me}_3\text{SiCH}_2^-$. Carbanions, for example the allyl anion, add to dimethylsilene, but the reactions appear to be complex. We have interpreted the product ions as arising by addition to carbon to give initially a silyl anion rather than addition to silicon to form an α -silyl carbanion, but this cannot be considered certain. Attempts to characterize dimethylsilene by its cycloaddition reactions have also met with only modest success. Although self-condensation and reaction with O_2 (both known reactions of dimethylsilene) have been demonstrated, neither of these cycloadditions could be studied in any detail.

Dimethylsilylene, $(\text{CH}_3)_2\text{Si}$, has been characterized by formation of an adduct with F^- (eq 39) and an $M-1$ ion with NH_2^- (eq 40). Each ion reacts further in ways which appear consistent with its postulated structure.

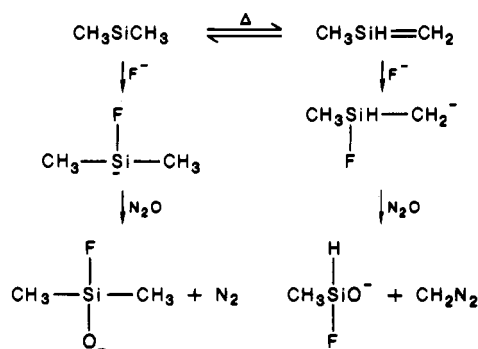


The acidity of dimethylsilylene has been determined by the bracketing technique to be near that of methanol ($381 \text{ kcal mol}^{-1}$). Considering its relatively high basicity, its $M-1$ anion is remarkably unreactive with such standard reagents as N_2O and CO_2 . It does, however, react with CS_2 (eq 40).

(41) Damrauer, R.; DePuy, C. H.; Davidson, I. M. T.; Hughes, K. J. *Organometallics* 1986, 5, 2050.

(42) Damrauer, R.; DePuy, C. H.; Davidson, I. M. T.; Hughes, K. J. *Organometallics* 1986, 5, 2054.

Scheme I



It is known from previous studies that dimethylsilylene and methylsilylene interconvert at high temperatures.³⁸ We have used ion-molecule reactions to probe the extent that this isomerization occurs under our pyrolysis conditions. Since addition of F^- to dimethylsilylene generates a silyl anion while addition of F^- to methylsilylene generates an α -silyl carbanion, we used the reaction with N_2O to distinguish these two product ions (Scheme I). At the lowest temperature at which pyrolysis occurs only products from dimethylsilylene are observed. As the pyrolysis temperature is raised, product ions expected from methylsilylene appear. At the highest temperatures that we could study we observed ions corresponding to a mixture of the two isomers with methylsilylene slightly predominating.

Concluding Remarks

We have tried to show in this Account that the anion chemistry of organosilicon compounds in all its rich diversity can be studied in the gas phase as well as (and often more easily than) in solution. Silyl anions, α -silyl carbanions, pentacoordinate silyl anions, and other ionic species can be generated, and their chemical properties investigated. In addition, the reactions of neutral organosilicon compounds, including highly unstable species like silenes and silylenes, with anions of all types, can be studied. We have found that the same general mechanistic principles apply to these gas-phase ion reactions as to analogous reactions in solution so that new reactions discovered for silicon compounds and their anions in the gas phase should also occur under more conventional reaction conditions. In addition, pentacoordinate silyl anions, which are usually thought of as transient intermediates, can be stable species in the gas phase whose chemical and physical properties are amenable to investigation. Gas-phase ion chemistry should, therefore, be useful as an adjunct to chemistry in solution for future studies of organosilicon chemistry.

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