Nucleophilic Reactions with Tetramethoxysilane and Tetraethoxysilane under Negative Ion Chemical Ionization Conditions

Vemisetty S. Murthy and Jack M. Miller*

Department of Chemistry, Brock University, St. Catharines,
Canada L2S 3A1

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Introduction

The formation and structure of hypervalent silicon compounds continue to be an area of lively interest. Although silicon compounds with coordination number greater than 4 have been known in solution for many years,[1] their study in the gas phase is more recent.[2] One impetus for these studies arises from the widespread use of nucleophilic activation and catalysis in the application of organosilicon compounds in organic synthesis.[3]

An important issue involves the possible influence of the low-lying vacant Si d orbitals on the properties and reactivity of silicon-containing compounds. A familiar example of d-orbital participation is the tendency of silicon to form pentavalent anions.[4] The ease of base-catalyzed reactions makes the negative ion silicon chemistry more difficult to study in solution than that of carbanions. The study of the silicon anion chemistry in the gas phase[5] (in the abscence of solvent) could make a contribution to the understanding of this important area of study in solution.

We recently demonstrated the formation of some interesting multiply bonded silicon–oxygen anions[6] and of pentavalent silicon anions[7] in the gas phase during an OR^- nucleophilic reaction on siloxane, $Si(OR')_4$ ($R' = CH_3$, Et) in the presence of an argon buffer gas, using the chemical ionization (CI) source of our Kratos Concept IS mass spectrometer. The extension of the work is presented here showing some interesting fragmentation and rearrangement reactions found during our study.

Experimental Section

The Kratos Concept IS double-focusing mass spectrometer used has an *E/B* configuration (Kratos Analytical, Urmston, Manchester, U.K.). The instrument was originally controlled by a Kratos DS90 Data General Eclipse based computer system. The Kratos Mach 3 data system running on a SUN SPARCstation was used for further data workup. While our work was in progress, we upgraded our DS-90 data system to the Mach 3 based Dart system. All the data were acquired at 10 s/dec and resolving power of ~1000.

The OR^- was generated from RONO by transesterification[8] of isoamyl nitrite and the appropriate ROH, using a reactor installed in the GC oven of the mass spectrometer. A 100 mL flask was used for the reactor with a glass to metal seal and appropriate fittings for a capillary connection. The flask was connected to the chemical ionization (CI) source via the GC re-entrant by a 1 m deactivated silica capillary (0.075 mm i.d. and 0.19 mm o.d.). A 10 mL portion of isoamyl nitrite and 100 mL of the appropriate ROH were injected into the flask at 25 °C through a rubber septum. The vacuum of the mass spectrometer ion source was allowed to draw the vapor of the nucleophile ($RONO \rightarrow RO^- + NO$) into the ion source.

The argon buffer gas necessary for these studies was admitted to the source via the CI reagent gas system (99% purity, Linde, Union Carbide Canada Limited). Ion source conditions: temperature, 150 °C; ionization energy, 180 eV; emission current, 300 mA.

We used an accelerating voltage of 6 kV. The source housing pressure with the argon buffer gas turned on was 5×10^{-4} Torr.

In *B/E* scans, used to determine daughter fragments of a particular ion, the instrument is tuned to the mass of the precursor of interest, and the ratio of magnetic field *B* to electrostatic analyzer voltage *E* is held constant as *B* is scanned. The resulting spectra should then contain all the daughters arising from the ion to which the instrument was tuned. The analogous B^2E scan determines the precursor ions leading to the mass to which the instrument was initially tuned.

The collision gas used during the *B/E* linked scan collision-induced dissociation (CID) experiments was helium. An ~1 mL sample of silicon substrate was added through the 75 mL heated reservoir probe[9] using the EI/CI probe lock. CID experiments, involving the interaction of the energetic (6 kV) ion with inert gas molecules in the first field free region of the instrument, enhance the sensitivity compared to that of observations of unimolecular decompositions.

Results and Discussion

The relative ion abundances in the spectra, for the reactions of OR^- ($R = CH_3$, CD_3, Et) with $(OR')_4Si$ ($R' = CH_3$, Et) are shown in Table 1. The S_N2 attack of OR^- on $(OR')_4Si$ leads to the formation of a pentacoordinate silicon anion adduct, A, $[(M + OR^-)]$ where $M = Si(OR')_4$ (Table 1).[10] Such pentacoordinate species in the gas phase are usually thought to have a trigonal bipyramidal geometry.[11] The *B/E* linked scan CID spectra of A (in all cases) showed that the pentacoordinate species reverted to a tetrahedral species by the elimination of ROR′ and R′OR′ as neutrals.[6] Bowie and co-workers[11] reported an exclusive nucleophilic displacement at carbon, for a specific case of $OCD_3^-/(CH_3)_3SiOCH_3$ under ion cyclotron resonance (ICR) conditions, leading to the formation of a $(CH_3)_3SiO^-$ tetrahedral anion. We found in the *B/E* CID spectra of $ROSi(OR')_4^-$ the formation of OR'^- due to the elimination of a neutral $ORSi(OR')_3$. We also found during the reaction of $OCH_3^-/(OCH_3)_4Si$ a simple elimination of MeOH from two –OMe groups on pentacoordinate silicon (*m/z* 183), leading to the α-siloxy carbanion $(OCH_3)_3SiOCH_2^-$ (*m/z* 151). We confirmed the loss of MeOH from the *m/z* 183 species by the B^2/E CID of $(OCH_3)_3SiOCH_2^-$.

The formation of A1 (Table 1) could be explained by two mechanisms: (i) the attack of the displaced OR'^- ligand on neutral $(OR')_4Si$; (ii) the participation of a pentacoordinate

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* Author to whom correspondence should be addressed.

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Table 1. Relative Ion Abundances in the Partial Spectra for the Reaction between RO$^-$ (from RONO) and M [M = Si(OR$'$)$_4$$^•$; A = (M + RO)$^-$; A1 = (M + R$'$O)$^-$]

		relative abundance										
R	R$'$	RO$^-$	A	A1	(M + H)$^-$	(M − H)$^-$	(A − ROR$'$ $^-$)	(A − R$'$OR$'$ $^-$)	[(M + H) − HCHO]$^-$	(M + H) − MeOH + HCHO	[(A − ROR$'$) − CH_2=CH_2]$^-$	[(A − R$'$OR$'$) − CH_2=CH_2]$^-$
Me	Me	100	44		23	1	9		3	2		
CD_3	Me	100	46	9	24 2[a]	1	11	2	3	2		
Et	Me	100	43	2	4	1	8	1	1	2		1
Me	Et	100	13	4	1		4	3			1	1
CD_3	Et	100	9	3	1[a]		4	3			1	1
Et	Et	100	10				3				1	

[a] (M + D)$^-$.

silicon anion, (OR$'$)$_4$SiOR$^-$, in a ligand exchange with a neutral (OR$'$)$_4$Si. We recently reported[7] such ligand exchange on $CH_3OSi(OEt)_4^-$ for the generation of $(OEt)_5Si^-$ and $(OCH_3)_2Si(OEt)_3^-$ ions during our study on the formation of the pentavalent silicon anions in the gas phase. Bartmess and coworkers[12] also reported such ligand exchange reactions during their study on the gas phase ion−molecule chemistry of borates and boronate esters.

The spectra summarized in Table 1 showed an intense (M + H)$^-$ ion formation except when R, R$'$ = Et. The formation of (M + H)$^-$ is due to the attack of H$^-$ on the siloxane.[7] This is confirmed by the spectra of the OCD_3^- reaction with (OR$'$)$_4$Si in which a shift of 1 amu [(M + D)$^-$] is observed. However, for the reaction of OCD_3^-/(OMe)$_4$Si, the B^2/E CID of (M + D)$^-$ (*m*/*z* 154) showed a parent ion at *m*/*z* 186. As mentioned, the loss of MeOD from the pentacoordinate species (OMe)$_4$SiOCD$_3^-$ leads to the formation of the ion at *m*/*z* 154. The generation of H$^-$ from OCH_3^- is known[7,12] and has been observed in reactions between OCH_3^- and Lewis acids.[13]

The *B*/*E* CID spectra of the (M + H)$^-$ ion (*m*/*z* 153) for the reaction of OCH_3^-/(OMe)$_4$Si showed some interesting fragmentation reactions. The formations of the siloxide ion (*m*/*z* 137, 24%) and silanion (*m*/*z* 121, 100%) from the *m*/*z* 153 species are due to the losses of CH_4 and MeOH, respectively. The readily available H on silicon can easily facilitate its reaction with CH_3 or OCH_3[10] to form CH_4 and MeOH. The *B*/*E* CID spectra of (M + D)$^-$ from the OCD_3^-/(OMe)$_4$Si reaction also showed an ion at *m*/*z* 137 (8%) which is due to the loss of a labeled methane (CH_3D).

During the *B*/*E* CID of the *m*/*z* 153 species from the OCH_3^-/(OMe)$_4$Si reaction, we also found a hydride migration to the central silicon followed by HCHO elimination, leading to the formation of a dihydride, $H_2Si(OMe)_3^-$ (*m*/*z* 123, 13%). We confirmed this reaction channel by *B*/*E* CID of the *m*/*z* 154 ion from the OCD_3^-/(OMe)$_4$Si reaction which confirms the loss of DCDO due to the D$^-$ migration (*m*/*z* 122, 19%). This H$^-$ migration is rather unusual in gas phase silicon anion chemistry. It probably involves a six-coordinate intermediate. However, such a gas phase H$^-$ transfer to boron is known during the reaction of OCH_3^- with Me$_2$BOMe.[14] We find that H$^-$ transfer to silicon is completely absent in the *B*/*E* CID spectra of A and A1 (Table 1). However, similar hydride transfer is seen in the positive ion spectra of some alkoxysilanes.[15]

The *B*/*E* CID of the *m*/*z* 154 ion showed some other interesting features. The intense ion at *m*/*z* 123 (38%) in the spectra is due to the loss of DCHO from the *m*/*z* 154 ion and indicates the occurrence of an H/D exchange between the D atom and OMe on silicon. It is known[11] that the nucleophilic displacement reaction on tetravalent silicon in solution proceeds with either an inversion or a retention of configuration. By analogy with pentavalent phosphorus, this is due to a facile interconversion of apical and equatorial substituents of the pentavalent silicon by either pseudorotation or turnstile rotation or via expansion of coordination via an octahedral intermediate. An interconversion of the apical and equatorial substituents on the pentacoordinate silicon anion may thus occur in the gas phase.[15]

The ion at *m*/*z* 91 (100%) in the *B*/*E* CID spectra of the *m*/*z* 154 species is due to the elimination of MeOD followed by HCHO loss. This transition also supports the attack of D$^-$ on (OMe)$_4$Si during the OCD_3^-/(OMe)$_4$Si reaction. We do not find any ions at *m*/*z* 121 or 124 in the *B*/*E* CID spectra of the *m*/*z* 154 species corresponding to the alkane losses, i.e., the loss of CD_3CH_3 and CH_3CH_3, respectively. This confirms that the formation of the ion at *m*/*z* 123 in the *B*/*E* CID spectra of (M + H)$^-$ (*m*/*z* 153) is due to the exclusive loss of HCHO via H$^-$ transfer.

The B^2/E CID spectra of (M − H)$^-$ (*m*/*z* 151) for the OR$^-$/(OMe)$_4$Si reaction showed that the ROSi(OMe)$_4^-$ pentacoordinate ion is the parent ion. This is due to the loss of MeOH from ROSi(OMe)$_4^-$. However, alkoxide anions are also strong bases. Hence, there may be a contribution to the formation of (M − H)$^-$ in the *B*/*E* spectra of the OR$^-$/(OMe)$_4$Si reaction by the abstraction of a proton from neutral siloxane.[11] We found that the (M − H)$^-$ ion is absent in the spectra of the OR$^-$/(OEt)$_4$Si reaction.

The *B*/*E* CID spectra of (M − H)$^-$ (*m*/*z* 151) showed an olefin loss with the elimination of CH_2=CH_2 (*m*/*z* 123).[6] A single and a double H$^-$ transfer (binary hydride transfer) to central silicon by the elimination of one (*m*/*z* 121) and two (*m*/*z* 91) HCHO molecules are also observed in the spectra.

The formation of $(OMe)_3SiO^-$ (*m*/*z* 137) during the OR$^-$/(OMe)$_4$Si reaction is due to the loss of ROCH$_3$ (A − ROR$'$) (Table 1). We recently reported the formation of $MeOSiO_2^-$ and $MeSiO_2^-$ ions from $(OMe)_3SiO^-$ during the *B*/*E* CID of $(OMe)_3SiO^-$ due to the elimination of MeOMe and (MeOH + HCHO), respectively.[6] Another interesting fragmentation from the *m*/*z* 137 species is the loss of a $CH_3^•$ radical leading to $(OMe)_2SiO_2^-$ (*m*/*z* 122). Such methyl cleavages from even-electron ions are known under chemical ionization conditions.[6,17]

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A H^- transfer to silicon was also found in this case, via the elimination of HCHO leading to the $HSi(OMe)_2O^-$ (*m/z* 107) (Table 1).

Conclusions

These interesting fragmentation reactions occurring during the ion–molecule reactions of alkoxide anions with tetramethoxysilane and tetraethoxysilane show some correspondence[10] between the products and mechanisms of gas phase ion–molecule reactions of silicon and of the same reactions in solution. Examples of nucleophilic attack on siloxanes in solution are seen in their reaction with Grignard reagents and organolithiums. Other analogies can be seen in the base-catalyzed gelation of alkoxysilanes[18] and in the chemistry of aqueous silicates.[19] It is interesting that two areas of research in our laboratories, gas phase ion chemistry and catalyst formation via sol–gel methods, have an area of potential overlap.

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