FORMATION OF $CH_3SiO_2^-$, $CH_3OSiO_2^-$, $HOSiO_2^-$ AND $HOSiO_2CH_2^-$ ANIONS IN THE GAS PHASE

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ABSTRACT

Multiply bonded silicon-oxygen anions, $CH_3SiO_2^-$ $CH_3OSiO_2^-$ $HOSiO_2^-$ and $HOSiO_2CH_2^-$ are formed during the nucleophilic reaction of RO^- (R= CH_3, C_2H_5) with tetramethoxysilane, $(CH_3O)_4Si$ and tetraethoxysilane, $(EtO)_4Si$ in the gas phase. The formation of such reactive species in the gas phase may be useful in the search for good reaction models in solution chemistry.

INTRODUCTION

There is widespread interest in compounds containing multiply bonded silicon (1) and numerous efforts to generate and characterize these elusive species have been described (2). Parallel efforts in the theoretical community have provided a fascinating picture of silicon-oxygen, silicon-carbon, and silicon-silicon multiple bonds, and have initiated an interesting debate concerning the relative stabilities of the corresponding silylene tautomers (3). Such species are usually highly reactive and as a result their chemistry is complex to study (4).

Anions containing multiply bonded silicon are known to form on photolysis of suitable substrates in an argon matrix (5). Thus, Brauman and co-workers (6) reported the formation of the dimethylsilanone enolate ion, $CH_3SiOCH_2^-$, by photodissociation of the trimethylsiloxide anion, $(CH_3)_3SiO^-$. Squires and co-workers (7) also reported the formation and reactivity of the dimethylsilanone enolate ion in the gas phase by collision-induced dissociation (CID) of $(CH_3)_3SiO^-$ ion in an ion cyclotron resonance (ICR) spectrometer. The formation of boron anions with boron multiply bonded to oxygen in a CI source has also been reported (8).

Many workers (9) have made the analogy between photochemistry and gas phase ion chemistry, and following on from these observations, we have attempted to observe the formation of such multiply bonded silicon-oxygen anions in the gas phase. We used argon as a buffer gas (5,10) and the chemical ionization (CI) source of our Kratos Concept IS mass spectrometer. We present results on the formation of four interesting multiply bonded silicon-oxygen anions, i.e. $CH_3SiO_2^-$ (**1**), $CH_3OSiO_2^-$ (**2**), $HOSiO_2^-$ (**3**) and $HOSiO_2CH_2^-$ (**4**).

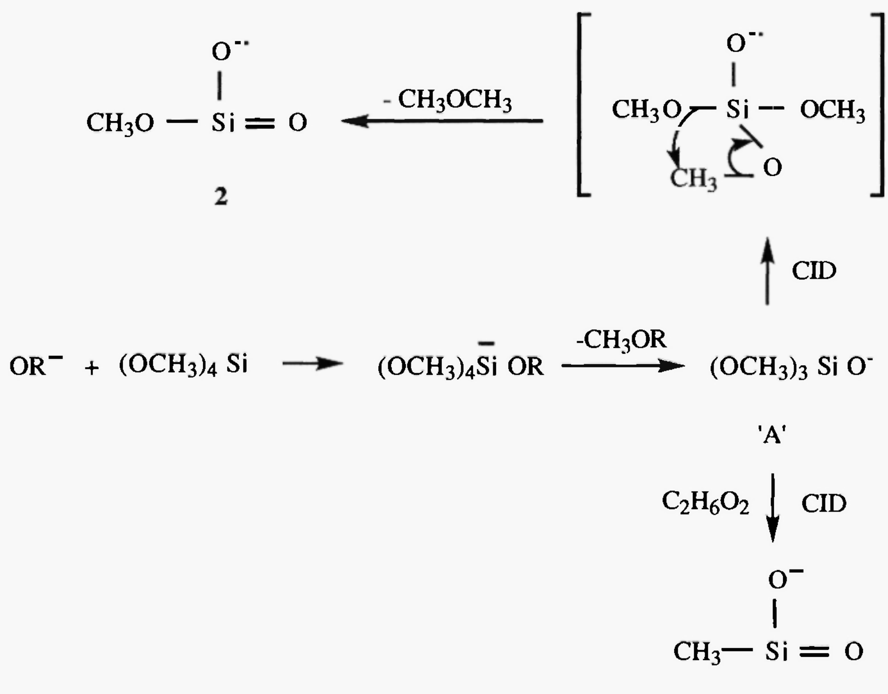
EXPERIMENTAL

The OR^- ion was generated from RONO, which was produced by transesterification (11) of isoamylnitrite 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 to the chemical ionization source, via the GC re-entrant. A deactivated fused silica capillary of 1 meter length, 0.075 mm i.d. and 0.19 mm o.d. was used for the connection. 10 µl of isoamyl nitrite and 100 µl of appropriate ROH are injected into the flask at 25^0 C, through a rubber septum. The vacuum of mass spectrometer drew the RONO vapour into the ion source where RO^- and NO were formed.

The Kratos Concept IS -double-focusing mass spectrometer used has an E/B configuration (Kratos Analytical, Urmston, Manchester, UK). 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 and also used the new system. All the data were acquired at 10 sec/dec and resolving power of *ca*1000. The spectra were acquired by multiple runs, at various time intervals on different days.

The argon buffer gas was admitted to the source via the CI reagent gas system. (99.996% purity, Linde, Union Carbide Canada Limited.) The ion source conditions were: temperature: 150^0 C; ionizing electron energy: 180 eV; emission current: 300 μA. We used an accelerating voltage of 6 kV. The source housing pressure with the argon buffer gas turned on was 5x 10^{-4} Torr. This gave a significant enhancement (10) of the negative ion current. When we further increased the total pressure by increasing the argon flow, a substantial fall off in the TIC was found. This is caused by the scattering of the ion beam due to the excessive argon pressure. We found no formation of interesting ions when we carried out the experiments in the absence of argon. The collision gas used during the B/E linked scan (CID) experiments was helium. ~1 μl of the silicon containing substrate was added through the 75 ml heated reservoir probe (12) using the EI/CI probe lock.

Tetramethyl orthosilicate, tetraethyl orthosilicate and isoamyl nitrite were purchased from Aldrich Chemical Co., Milwaukee, WIS, USA; the purities were 98, 99 and 97 % respectively. Methanol-d_4 was of 99.8 atom % D and was purchased from Isotec inc. Miamisburg, OH, USA. All the compounds were used directly without any further purification.



Scheme 1

RESULTS AND DISCUSSION

The anions **1** and **2** have been generated by collision-induced dissociation (CID) of the trimethoxysiloxide anion, $(CH_3O)_3SiO^-$ (A), and **3** and **4** are generated by CID of the ethoxydihydroxysiloxide anion, $EtO(OH)_2SiO^-$ (B). The anion **4** has also been formed by CID of the diethoxyhydroxysiloxide anion, $(EtO)_2OHSiO^-$ (C). The anion 'A' was initially formed from a pentacoordinate silicon anion intermediate formed by a bimolecular reaction of an alkoxide anion, OR^- (R= CH_3,CD_3,Et), with tetramethoxysilane (Scheme 1). Support is given by the major ions in the spectrum (13) resulting from the reaction of tetramethoxysilane and CH_3O^- (Fig. 1), i.e., $[Si(OMe)_5]^-$ (m/z 183), $[HSi(OMe)_4]^-$ (m/z 153), $[(MeO)_3SiO]^-$ (m/z 137) and $[H_2Si(OMe)_3]^-$ (m/z 123). In contrast, anion 'B' is formed by elimination of two ethylene units from $[Si(OEt)_5]^-$. Anion 'C' was formed via the reaction of OEt^- with tetraethoxysilane, by the loss of EtOEt and C_2H_4.

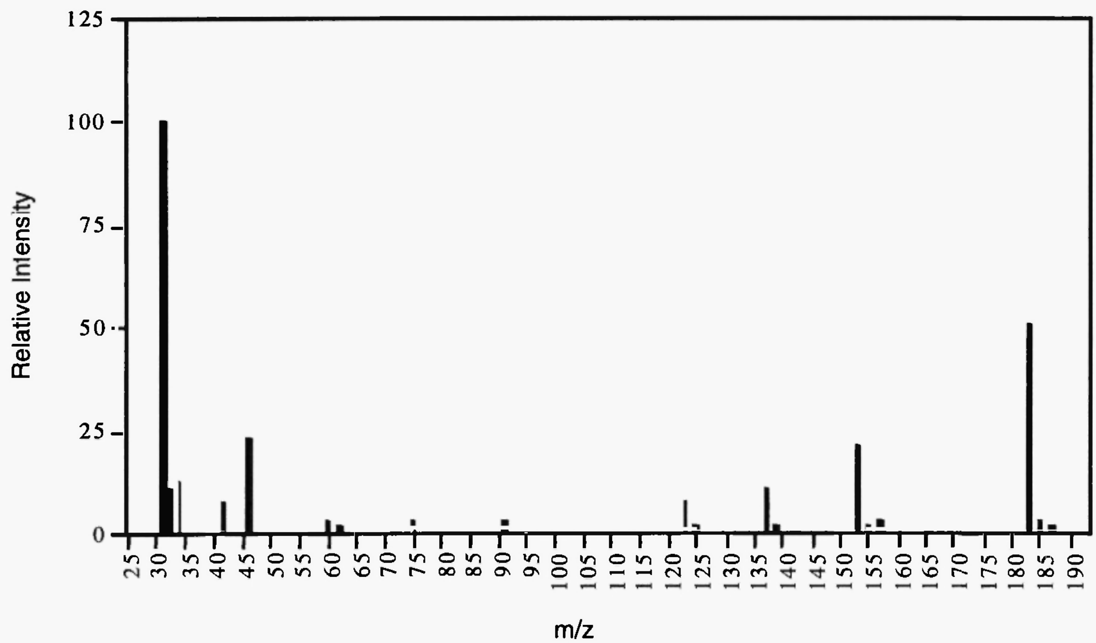
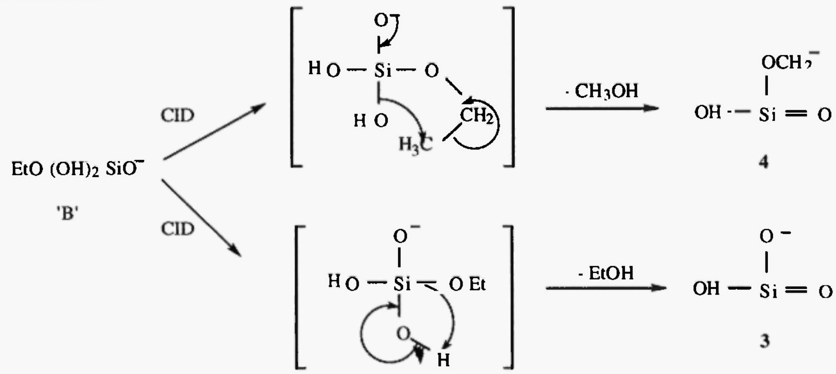


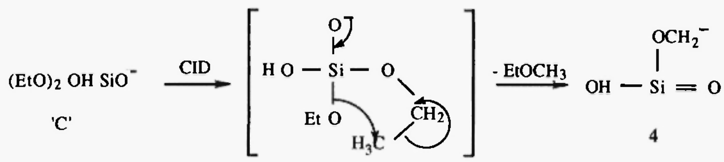
Fig. 1 Mass Spectrum produced by the reaction between tetramethoxysilane, $(OMe)_4Si$ and OCH_3^-.

The S_N2 displacement (4) of OR^- on tetramethoxysilane leads to the elimination of CH_3OR and formation of the precursor ion 'A' (m/z137). When R= CD_3 or Et , we have also found the loss of a CH_3OCH_3 neutral from the pentacoordinate silicon anion intermediate leading to the formation of $(CH_3O)_2(CD_3O)SiO^-$ (m/z 140) or $(CH_3)_2(EtO)SiO^-$ (m/z 151) ions. CID of 'A' yielded a number of product ions (13) including **1** (m/z 75) Oand **2** (m/z 91). The formation of **1** involves the loss of $C_2H_6O_2$ possibly as HCHO and MeOH or to two successive losses of $CH_3O^{\cdot}$ moieties from 'A', (Scheme 1). The tendency towards strong Si-O bond formation and the preference of Group IV organometallics for three coordination in the positive ion mass spectra support the postulation of structure **1** as shown.



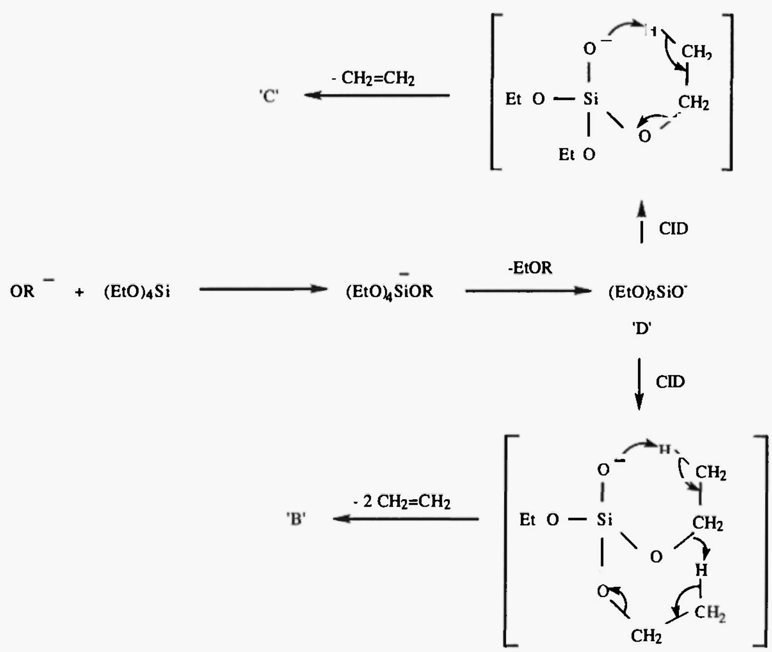
Scheme 2

Squires and co-workers (7) prepared the $CH_3SiO_2^-$ anion (1) by a bimolecular reaction between the dimethylsilanone enolate ion, $CH_3SiOCH_2^-$ and CO_2. We found as did these workers, that **1** fragments by loss of methyl to form SiO_2^- (m/z 60) (Fig. 1).



Scheme 3

The formation of **2** can be explained by the loss of CH_3OCH_3 from 'A' (14) (Scheme 1). We have confirmed this reaction channel by the CID (B/E) of $(OCH_3)_2(OCD_3)SiO^-$ and $(OCH_3)_2(OEt)SiO^-$ ions; the former eliminates CD_3OCH_3 and the latter eliminates $EtOCH_3$, in both cases to form $CH_3OSiO_2^-$ (**2**). We cannot exclude the possibility of losses of $CH_3O^{\cdot}$ and $CH_3^{\cdot}$ rather than the loss of dimethyl ether, but the presence of a peak in the mass spectrum at m/z 46 is indicative of the formation of the ether.



Scheme 4

The CID of 'B' (m/z 123) yields two daughter ions, **3** (m/z 77) and $HOSiO_2CH_2^-$ enolate ion (**4**) (m/z 91) (scheme 2). The formation of **3** is due to the loss of EtOH (14) similar to loss of CH_3OCH_3 observed in the formation of **2**. The formation of **4** arises by the loss of CH_3OH from 'B'. A similar mechanism could also explain the formation of **4** from 'C' (m/z 151) by the elimination of a neutral $EtOCH_3$ from the two adjacent -OEt groups on silicon atom in 'C' (Scheme 3).
The ions 'B' and 'C' are formed on CID of $(EtO)_3SiO$- ('D', m/z 179) by olefin eliminations (Scheme 4, as reported in (7)). The ion 'D' is the S_N2 reaction product from $(EtO)_4Si$ and OR^-. We explain these olefin losses as occurring by single ('C') and double ('B') cyclic elimination mechanisms, which are similar to ester pyrolysis (15). Froelicher et al. (7) also reported similar olefin loss during the reaction of dimethylsilanone enolate ion with ROH (R= Et, i-Pr). This occurs via a single cyclic elimination mechanism leading to the formation of the silanone hydrate anion, $(CH_3)_2(OH)SiO^-$.

The results of the studies of the formation of multiply bonded silicon-oxygen anions in the gas phase, and the occurrence of analogous reactions in photo(solution) chemistry may provide some clues in establishing a closer relationship (16) between these two chemistries. The formation and the study of such reactive species in the gas phase may be useful in the search for good reaction models for solution chemistry. Corriu's group has reported evidence in solution for some of the hypercoordinated species discussed and have chemically isolated related species (17, 18). We are following up these studies with further work on the heavier analogues, germanium and tin. The mass spectral investigations may provide a clue towards species which may be found in solution.

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