The Mechanism of the Collision-induced Loss of Methane from the Trimethylsilyl Negative Ion

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Collisional activation of Me_3Si^- induces major losses of $H^\cdot$, H_2, and CH_4. Loss of H_2 forms deprotonated dimethylsilene, *ab initio* calculations (6-31 + G) indicate the structure of the product to be $Me-Si\overset{\diagup CH_2}{\underset{\diagdown CH_2}{-}}$.
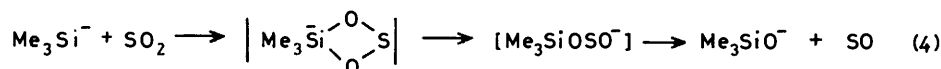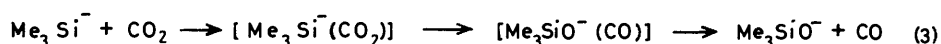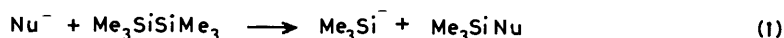
Loss of methane could, in principle, occur by two ionic pathways, *viz.* (i) by initial formation of an incipient hydride ion which then removes a methyl cation by an S_N2 process, or (ii) by formation of a bound methyl anion which effects deprotonation of a methyl group. *Ab initio* calculations suggest that the latter process is more energetically favoured and that the lowest energy pathway is the concerted route $Me_3Si^- \longrightarrow [Me^-(Me_2Si)]\dagger \longrightarrow Me\bar{S}i=CH_2 + CH_4$.

The ion Me_3Si^- is best prepared by the $S_N2(Si)$ reaction between a Nu^- ($Nu = F$, HO, MeO, NH_2) and hexamethyldisilane [equation (1)].[1] It cannot be made by reaction between a strong base (*e.g.* HO^- or NH_2^-) with trimethylsilane, since such a reaction produces an α-silylcarbanion [equation (2)].[1,2] The ion Me_3Si^- is not a powerful nucleophile. For example, it undergoes an S_N2 reaction with methyl chloride to yield Cl^- with a reaction efficiency of 0.1 (*i.e.* reaction proceeds for one in every ten collisions).[3] For comparison, the reaction efficiencies of $CH_2=CH_2-CH_2^-$ and HO^- with methyl chloride are 0.2 and 1.0 respectively.[4,5] The chemistry of Me_3Si^- is dominated by the tendency of silicon to form strong bonds to oxygen, nitrogen, and sulphur. Thus Me_3Si^- reacts with CO_2, COS, CS_2, SO_2, and N_2O by oxygen or sulphur transfer.[6] The reaction mechanism can be complex; see, for example, reactions with CO_2 and SO_2 [equations (3) and (4)].

meter operating at 70 eV in the negative chemical ionization mode. Me_3Si^- was formed as shown in equation (1) using HO^- as the reactant ion; helium was used as collision gas. Full details are provided in the Experimental section. *Ab initio* calculations were carried out using GAUSSIAN 82[11] at the 6-31 + G level. Procedures used for these calculations have been reported in full previously.[6,12]

The c.a. mass spectrum of Me_3Si^- is shown in Figure 1. The various fragmentations are summarised in the Scheme; of these the major fragmentations are the competitive losses of $H^\cdot$, H_2, and CH_4.

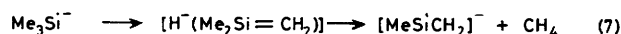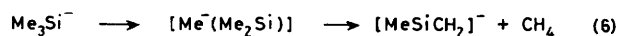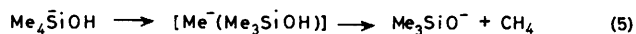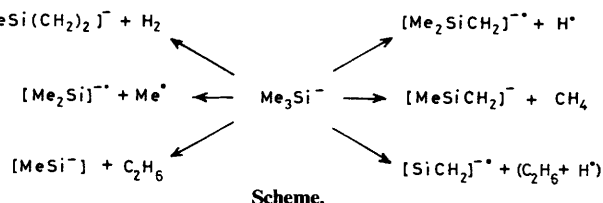*The Loss of CH_4 from Me_3Si^-.*—Collision-induced loss of methane occurs from a variety of organosilicon negative ions including Me_3SiO^-,[7,10] α-silylcarbanions $Me_3Si\bar{C}HR$ ($R =$

$$Nu^- + Me_3SiSiMe_3 \longrightarrow Me_3Si^- + Me_3SiNu \qquad (1)$$

$$NH_2^- + Me_3SiH \longrightarrow {}^-CH_2Si(Me)_2H + NH_3 \qquad (2)$$

$$Me_3Si^- + CO_2 \longrightarrow [Me_3Si^-(CO_2)] \longrightarrow [Me_3SiO^-(CO)] \longrightarrow Me_3SiO^- + CO \qquad (3)$$

$$Me_3Si^- + SO_2 \longrightarrow \left| Me_3\bar{S}i\overset{O}{\underset{O}{\diagup \diagdown}}S \right| \longrightarrow [Me_3SiOSO^-] \longrightarrow Me_3SiO^- + SO \qquad (4)$$
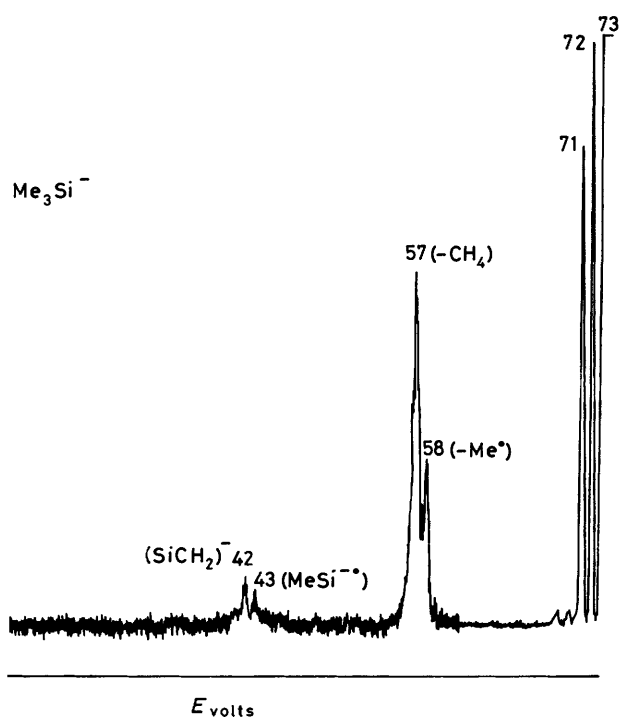
In this paper we describe the collisional-induced fragmentations of Me_3Si^-. We were particularly interested to determine whether elimination of radicals or neutrals from Me_3Si^- could form (i) mono- or di-co-ordinate silicon negative ions, or (ii) multiply bonded silicon anions, a subject of much current interest.[1,7-10]

Results and Discussion

Collisional activation (c.a.) mass spectra reported in this paper were measured with a Vacuum Generators ZAB 2HF spectro-

$$Me_4\bar{S}iOH \longrightarrow [Me^-(Me_3SiOH)] \longrightarrow Me_3SiO^- + CH_4 \qquad (5)$$

$$Me_3Si^- \longrightarrow [Me^-(Me_2Si)] \longrightarrow [MeSiCH_2]^- + CH_4 \qquad (6)$$

$$Me_3Si^- \longrightarrow [H^-(Me_2Si=CH_2)] \longrightarrow [Me\bar{S}iCH_2]^- + CH_4 \qquad (7)$$

alkyl, vinyl, or aryl),[10] and penta-co-ordinate silicon species including Me_4SiX ($X = F$, HO, or O alkyl).[2,12,13] All these reactions are thought to proceed through a methyl anion complex, see *e.g.* equation (5).[12] We chose to study the loss of methane from Me_3Si^- in detail, since it is possible that two ionic mechanisms may operate, *i.e.* reaction through initial formation of a methyl anion complex [equation (6)] or through an initial hydride ion complex [equation (7)]. These possibilities have been explored extensively by *ab initio* calculations at the 6-31 + G level; results are summarized in Figures 2 and 4. Structures and energies of reactants and products are given in Figure 3; structures of intermediates and barrier crests are indicated in Figures 2 and 4.

Scheme:

[MeSi(CH₂)₂]⁻ + H₂

[Me₂Si]⁻˙ + Me˙ ⟵ Me₃Si⁻ ⟶ [MeSiCH₂]⁻ + CH₄

[Me₂SiCH₂]⁻˙ + H˙

[MeSi⁻] + C₂H₆

[SiCH₂]⁻˙ + (C₂H₆ + H˙)

Scheme.

Figure 1. C.a. mass spectrum of Me_3Si^-. For experimental conditions, see Experimental section. When a voltage of +2 000 V was applied to the collision cell, the following collision-induced:unimolecular ratios were observed: [m/z (c:u)]; 72 (60:40), 71 (90:10), 58 (90:10), 57 (98:2), 43 (95:5), and 42 (100:0)

In Figure 2 are shown results for the reaction through an incipient methyl anion.* Surprisingly, the minimum-energy route (pathway I, Figure 2) is concerted (although not synchronous); other similar reactions that we have studied previously have all been stepwise.[12,14] A careful search has shown no intermediate corresponding to [$Me^-(Me_2Si)$] [cf. equation (6)] in this minimum-energy pathway; instead, the methyl anion can move away from silicon [to a distance (~ 4 Å) essentially equivalent to complete C–Si bond breaking] and into a conformation to effect concomitant deprotonation. Some activation of the transferring proton is required, but it is clearly small. The optimum positioning of the methyl anion leads to structure **A** at the crest of a barrier (295 kJ mol^{-1} above reactants) corresponding to a transition structure where the transferring proton is equidistant from carbons 1 and 2.† The minimum-energy pathway proceeds over this crest to products as shown. The structure of the product ion [$MeSiCH_2$]$^-$ is shown in Figure 3. The C–Si–C angle is 102.7°, and the $SiC(H_2)$ bond length of 1.78 Å is slightly longer than that of a normal SiC double bond [cf. the value of 1.71 Å for the Si=C bond of dimethylsilene (Figure 3 and cf. reference 15)]. Thus the negative charge resides primarily on silicon, and there is very little contribution from

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* There is also the possibility that the loss of methane might occur by a reaction involving a methyl radical, i.e. $Me_3Si^- \longrightarrow [Me^·(Me_2Si^-·)]$ $\longrightarrow [MeSiCH_2]^- + CH_4$. This is unlikely since the process Me_3Si^- $\longrightarrow Me_2Si^{-·} + Me^·$ is 84 kJ mol^{-1} more endothermic than Me_3Si^- $\longrightarrow Me_2Si + Me^-$ (see Figure 2). In addition, we identify the Me moiety in Figure 2 (e.g. formula **A**) as a methyl anion since calculations establish pyramidal geometry.

† A reviewer has asked whether the third methyl group plays any part in this reaction. The affinity of Me^- for the remaining methyl group is low because of the lack of acidity of the methyl hydrogens. Thus the effect of the third methyl group will be insignificant.

resonance structure $MeSiCH_2^-$. The alternative decomposition pathway to Me^- plus Me_2Si is not observed experimentally, in accord with calculations (Figures 2 and 3) which indicate this reaction to be 257 kJ mol^{-1} more endothermic than formation of [$MeSiCH_2$]$^-$ and methane.

The minimum-energy pathway shown in Figure 2 is the concerted route I. Since previous cognate studies have always indicated stepwise processes,[12,14] it was of interest to determine whether high-energy stepwise pathways can pertain in this system. We have found such a process; it is shown as pathway II in Figure 2. Hydrogen-bonded complex **B** is reached after Me^- has circled out to 5.2 Å from silicon; it is clearly one of several possible conformations. The complex lies in a shallow potential minimum and has a large C^- to H distance (2.95 Å); the system proceeds through **C** to products as shown. From an experimental point of view this stepwise pathway is unlikely on two grounds, viz. (i) the barrier for pathway II is some 80 kJ mol^{-1} more endothermic than that of route I, and (ii) the stepwise process should compete with formation of Me^- (Figure 2), a process not observed experimentally.

The hydride ion mechanism is shown in Figure 4. It is less likely than the concerted mechanism shown in Figure 2 for a number of reasons, including the obvious one that the barrier for the hydride ion reaction is 440 kJ mol^{-1}, whereas that for the methyl anion reaction is 295 kJ mol^{-1}. Nevertheless, there are interesting features to the reaction sequences shown in Figure 4. Firstly, the elimination of methane is a stepwise reaction [cf. equation (7)]. The first barrier crest (370 kJ mol^{-1}) corresponds to **D**; the minimum-energy pathway then proceeds to intermediate ion complex **E** in which the hydride ion is positioned ready to effect the S_N2 reaction over **F** (440 kJ mol^{-1}) to products. Secondly, the reaction competes with two other processes. When the system proceeds over the barrier at **D**, deprotonation may occur (see later), but more interestingly, hydride ion transfer may form $^-CH_2Si(Me)_2H$.‡ Although the loss of methane shown in Figure 4 is less feasible energetically than that shown in Figure 2, the hydride ion transfer (Figure 4) should compete with the methane loss shown in Figure 2.

Since ab initio calculations indicate loss of methane from Me_3Si^- (Figure 2) could compete with the 1,2-hydride transfer reaction $Me_3Si^- \longrightarrow {}^-CH_2Si(Me)_2H$ (Figure 4), we must determine whether $^-CH_2Si(Me)_2H$ can itself eliminate methane. The c.a. mass spectrum of $^-CH_2Si(Me)_2H$ is completely dominated by loss of dihydrogen [equation (8)]; the loss of methane [equation (9)] is insignificant in comparison.§ Thus we propose that the loss of methane from Me_3Si^- occurs principally by the concerted route shown in Figure 2; other pathways are minor in comparison.

We have measured the deuterium kinetic isotope effect for the loss of methane from Me_3Si^-. The c.a. mass spectrum of $(CD_3)Me_2Si^-$ ¶ shows loss of $CH_4:CH_3D:CD_3H$ in the ratio 100:53:65. These figures can be interpreted in terms of a

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‡ 1,2-Hydride ion transfers in carbon systems are considered to be 'forbidden' because of orbital symmetry constraints, and there are no recorded examples in the condensed phase of 1,2-hydrogen migration along a carbon chain in carbanions.[16] The barrier for the degenerate 1,2-hydride shift in the ethyl anion is calculated to be 202 kJ mol^{-1},[17] but this cannot be checked experimentally since the ethyl radical has a negative electron affinity (-83 kJ mol^{-1}).[18] The calculated barrier for the 1,2-H conversion of Me_3Si^- into $^-CH_2Si(Me)_2H$ is 376 kJ mol^{-1} (see Figure 4).

§ The c.a. mass spectrum of $^-CH_2Si(Me)_2H$ [formed as in equation (2)] is [m/z (loss) %]; 72 (H$^·$) 45, 71 (H$_2$) 100, and 58 (CH$_4$) 1. Experimental conditions as for Figure 1 (see Experimental section).

¶ The c.a. mass spectrum of $(CD_3)Me_2Si^-$ is [m/z (loss) %]; 75 (H$^·$) 100, 74 (H$_2$, D$^·$) 82, 73 (HD) 22, 61 (Me$^·$) 15.0, 60 (CH$_4$) 25.9, 59 (CH$_3$D) 13.7, 58 (CD$_3$$^·$) 13.7, 57 (CD$_3$H) 16.8, 46 (C$_2H_6$) 0.3, 44 (C$_2H_6D^·$) 0.9, 43 (C$_2H_3D_3$) 0.5, and 42 (C$_2H_4D_3$$^·$) 2.0.
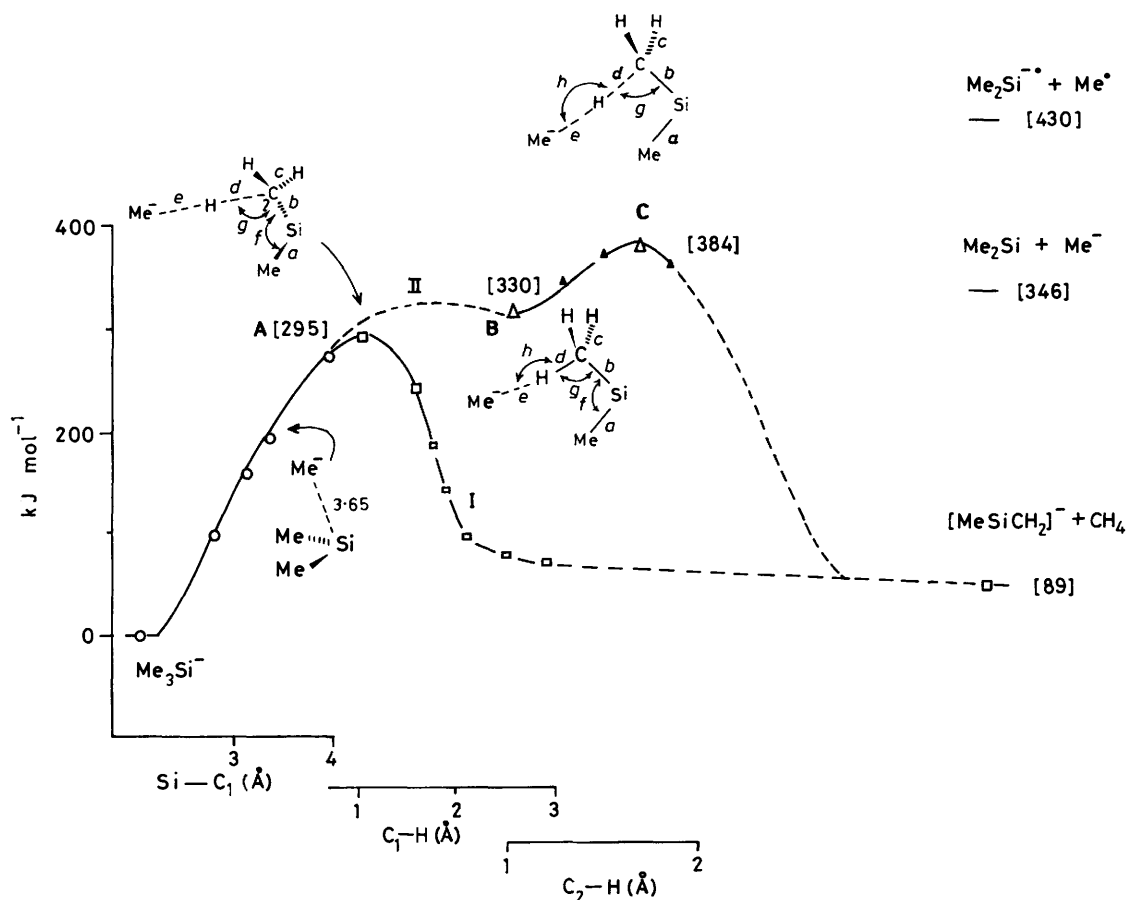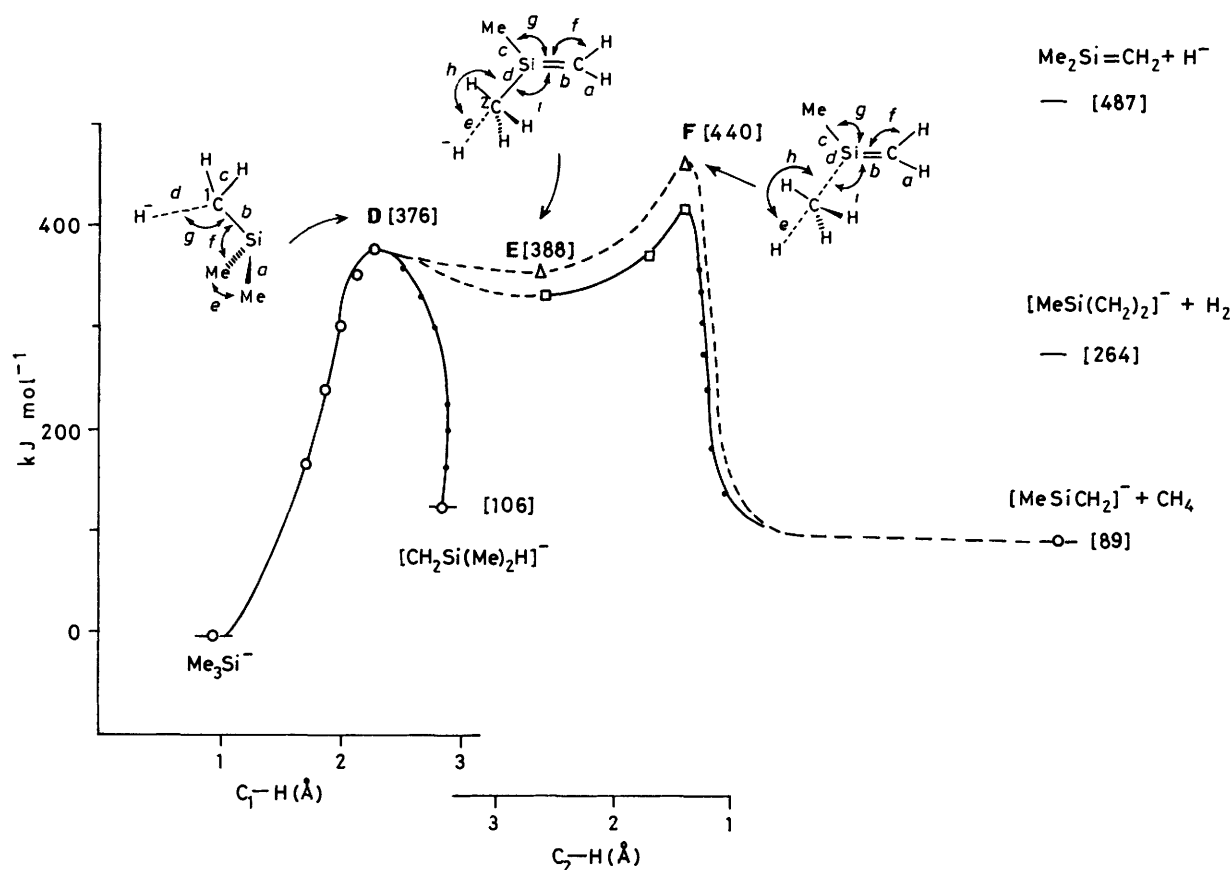
Figure 2. *Ab initio* results (6-31 + G) for the methyl anion-induced loss of methane from Me_3Si^-. Large points are fully optimized geometries in the direction of the appropriate reaction co-ordinate. Small points are derived from potential surface scans. Energies and geometries of reactant and products are listed in Figure 3. Energies and geometries of **A**—**C** are as follows [(Å), (°)]: **A**, ($-407.553\ 51$), $a = 2.00, b = 1.81, c = 1.08, d = 1.30, e = 1.32, f = 102, g = 115.5, C^--Si = 3.84$; **B**, ($-407.541\ 57$), $a = 1.97, b = 1.93, c = 1.09, d = 1.09, e = 2.95, f = 98.1, g = 113.3, h = 175.7$; **C**, ($-407.520\ 57$), $a = 1.99, b = 1.89, c = 1.09, d = 1.43, e = 1.50, g = 114.2, h = 176.8$
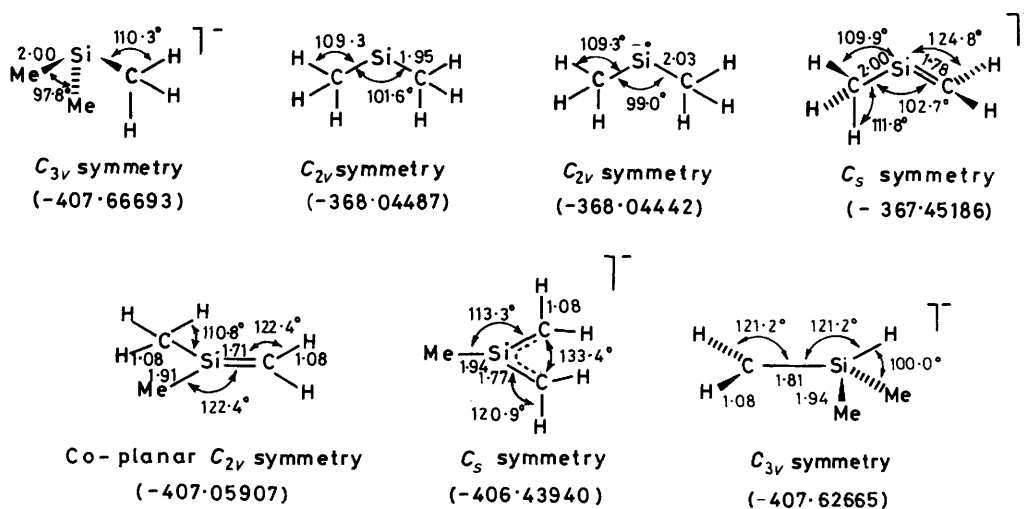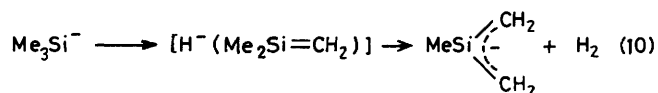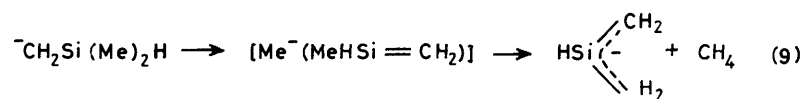

Figure 3. Geometries and energies of reactant and products shown in Figures 2 and 4

secondary isotope effect H/D of 1.10 (for the formation of incipient Me^- as opposed to CD_3^-) and a primary isotope effect of 1.9 (for removal of H^+/D^+). Such results seem consistent with the concerted mechanism shown in Figure 2. In contrast, reactions which involve initial hydride ion complexes show higher H/D effects. For example, losses of H_2 from EtO^- and MeO^- show experimental H/D values for the first step of reaction of 3 and 7.5 respectively.[19,20]

Figure 4. *Ab initio* calculations (6-31 + G) for the hydride anion induced loss of methane from Me_3Si^-. Large points are fully optimized geometries in

the direction of the appropriate reaction co-ordinate. The solid line ⊡—⊡—■ indicates calculations for the model system $H^-\binom{H}{Me}Si=CH_2$. The

dotted line △ .... △ indicates the results of calculations for the system studied experimentally, but in this case only reactive intermediate **E** and barrier crest **F** have been computed. Structures and geometries of reactant and product ions are shown in Figure 3. Energies and geometries of **D**—**F** are as follows [(Å), (°)]: **D**, (−407.524 93), $a = 1.93$, $b = 1.78$, $c = 1.075$, $d = 2.60$, $e = 109.3$, $f = 113.1$, $g = 105.7$; **E**, (−407.534 62), $a = 1.08$, $b = 1.73$, $c = 1.89$, $d = 1.89$, $e = 2.82$, $f = 122.7$, $g = 116.9$, $h = 177.0$, $i = 127.3$; **F**, (−407.499 22), $a = 1.08$, $b = 1.74$, $c = 1.94$, $d = 2.04$, $e = 1.90$, $f = 123.3$, $g = 113.5$, $h = 178.4$, $i = 129.7$

$$^-CH_2Si(Me)_2H \longrightarrow [H^-(Me_2Si=CH_2)] \longrightarrow MeSi\binom{CH_2}{CH_2} + H_2 \qquad (8)$$

$$^-CH_2Si(Me)_2H \longrightarrow [Me^-(MeHSi=CH_2)] \longrightarrow HSi\binom{CH_2}{H_2} + CH_4 \qquad (9)$$

$$Me_3Si^- \longrightarrow [H^-(Me_2Si=CH_2)] \longrightarrow MeSi\binom{CH_2}{CH_2} + H_2 \qquad (10)$$
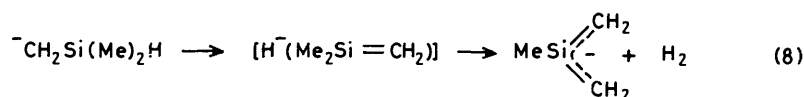
Other Losses from Me_3Si^-.—The other losses shown in the Scheme have not been fully explored by *ab initio* methods but some information is available in Figures 2—4. The minor loss of C_2H_6 clearly involves the formation of an incipient methyl anion (see Figure 2) followed by S_N2 attack at a second methyl group. The losses of $H^{\cdot}$ and H_2 have appreciable deuterium isotope effects [the ratio of losses of $H^{\cdot}:(D^{\cdot} + H_2):HD$ is 100:82:22]; exact values for each process cannot, of course, be derived. The loss of H_2 presumably proceeds initially to **D** (Figure 4). Separation of the hydride ion does not occur at this stage, since the formation of H^- and dimethylsilene is endo-

thermic by 487 kJ mol⁻¹ (Figures 3 and 4). Instead, the hydride ion effects deprotonation of a methyl group of dimethylsilene to yield $[MeSi(CH_2)_2]^-$ plus H_2 [equation (10), see also Figures 3 and 4]. Since Me_3Si^- can rearrange to $^-CH_2Si(Me)_2H$ over a barrier of 376 kJ mol⁻¹, it is conceivable that some of the H_2 loss in the spectrum of Me_3Si^- is coming from the rearranged ion to also form $[MeSi(CH_2)_2]^-$ [see equation (8)]. The computed structures of dimethylsilene and its deprotonated form $[MeSi(CH_2)_2]^-$ are shown in Figure 3. Dimethylsilene is a coplanar structure with Si–C and Si=C bond lengths of 1.91 and 1.71 Å respectively (*cf.* reference 15). The deprotonated form is also planar; the Me–Si bond is a standard single bond (1.94 Å), and the two $(H_2)CSi$ bonds are of equal length corresponding to slightly extended double bonds (1.77 Å).

In conclusion, mono- and di-co-ordinate silicon negative ions together with multiply bonded tri-co-ordinate silicon ions are

formed when Me_3Si^- is subjected to collisional activation. The most interesting reaction is loss of methane; a combination of experimental and *ab initio* results suggest this to be a concerted reaction in which a bound methyl anion deprotonates a methyl group. To our knowledge, this is the first report of a concerted decomposition of a polyatomic negative ion in which two bonds are broken.

Experimental

C.a. mass spectra were recorded on a Vacuum Generators ZAB 2HF mass spectrometer operating in the negative chemical ionization mode.[21] All slits were fully open to obtain maximum sensitivity and to minimize energy-resolution effects. The chemical ionization slit was used in the ion source; ionizing energy 70 eV (tungsten filament); ion source temperature 150 °C; accelerating voltage 8 kV. Me_3Si^- and $CD_3(Me)_2Si^-$ were formed by the nucleophilic displacement reaction between HO^- and $Me_3SiSiMe$ and $CD_3(Me)_2SiSi(Me)_2CD_3$ respectively. Reactant HO^- ions were formed from H_2O using 70 eV electrons.[22] The indicated source pressure of H_2O was 5×10^{-4} Torr. The $Me_3SiSiMe_3$ pressure (the substrate was introduced through the septum inlet at 150 °C) was 5×10^{-7} Torr. The estimated total pressure in the source is 10^{-1} Torr. The ion $^-CH_2Si(Me)_2H$ was formed from Me_3SiH (source pressure 5×10^{-7} Torr) and NH_2^- (from NH_3 with 70 eV electrons—pressure in source 5×10^{-4} Torr). The pressure of He in the second collision cell is 2×10^{-7} Torr, measured by an ion gauge situated between the electric sector and the second collision cell. This produced a decrease in the main beam signal of *ca.* 10% and thus corresponds to single collision conditions.

Dimethylsilane and trimethylsilane were commercial samples. Hexamethyldisilane was prepared by a standard method.[23]

$[1,1,1,2,2,2-^2H_6]$*Hexamethyldisilane.* $[^2H_3]$Methyl iodide (2.89 g) was added dropwise to magnesium turnings (54.4 mg) in anhydrous diethyl ether (4 ml) at 20 °C. The Grignard reagent was then added dropwise to a solution of 1,2-dichlorotetramethyldisilane[24] (1.84 g) in anhydrous diethyl ether maintained at 0 °C for 20 min, then heated under reflux for 30 min. The reaction mixture was washed with aqueous ammonium chloride (saturated, 2×5 ml), poured into concentrated sulphuric acid (3 ml) at 0 °C, and the upper layer separated and distilled to yield 1,2-bis(trideuteriomethyl)tetramethylsilane (0.72 g, 48%) as a colourless liquid, b.p. 112—114 °C at 760 mmHg.

Acknowledgements

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