The Mechanisms of Alkane Eliminations from the Intermediates produced by Reactions of the Hydroxide and Methoxide Negative Ions with Tetramethylsilane in the Gas Phase

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ab initio Calculations (6-21G level, GAUSSIAN 82) and both ion cyclotron resonance (i.c.r.) and flowing afterglow (F.A.) experiments have been used to study the reactions of HO^- and MeO^- with Me_4Si (and related systems). *ab initio* Calculations suggest that interconversion of apical and equatorial methyl groups in trigonal bipyramidal $[Me_2H_3Si^-]$ (formation energy -200 kJ mol^{-1}) occurs through a square pyramidal transition state (barrier 12 kJ mol^{-1}). Deuterium labelling (F.A.) studies show that for the fast reaction (1) the elimination of CH_4 is statistical: no deuterium isotope effect is observed.

$$HO^- + Me_4Si \longrightarrow Me_3SiO^- + CH_4 \qquad (1)$$

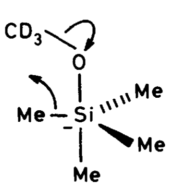
The MeO^- ion reacts with Me_4Si in i.c.r. experiments by two slow processes:

$$MeO^- + Me_4Si \longrightarrow Me_3SiO^- + C_2H_6 \qquad (2)$$

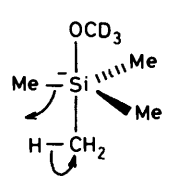
$$MeO^- + Me_4Si \longrightarrow Me_2(MeO)SiCH_2^- + CH_4 \qquad (3)$$

The latter process (3) is not observed in F.A. experiments and is likely to be formed from excited MeO^- species. *ab initio* Calculations for the model system MeO^-–$MeSiH_3$ suggest that reactions (1)—(3) are stepwise: the key step is cleavage of the Si–C bond in the reactive intermediate to produce a reacting solvated methyl anion. There are high internal barriers for reactions (2) and (3), and both secondary and primary (where appropriate) deuterium isotope effects are noted for these two reactions in i.c.r. experiments.

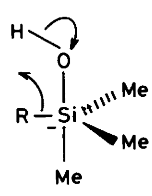
Flowing afterglow,[1,2] and ion cyclotron resonance[3] studies of the reactions between nucleophiles (*e.g.* F^-, HO^-, and MeO^-) and tetra-alkylsilanes indicate that reactive intermediates R_4Si^-Nu (thought to be of trigonal bipyramidal geometry) undergo 1,2-elimination† of neutral molecules. For example, the reaction of CD_3O^- with tetramethylsilane leads to competitive elimination of CH_4 and $MeCD_3$ [see the schematic representations (**1**) and (**2**)].[3] DePuy, Bierbaum, and Damrauer have reported[2] that a study of the competitive eliminations of RH and CH_4 from HO^-–Me_3SiR systems [see (**3**) for the elimination of RH] can be used to determine a gas-phase acidity scale for alkanes.[2] It is unlikely that such a correlation could be obtained unless the apical and equatorial substituents equilibrate prior to decomposition of the five-co-ordinate intermediate. Apical–equatorial interchange has been noted in the condensed phase[4] and it is has been suggested,[5] by analogy with the chemistry of pentavalent phosphorus, that this may be achieved either by pseudo-rotation[6] or turnstile rotation.[7] Analogous 1,2-elimination reactions in the gas phase have been observed for excited alkoxide ions[8,9] and from tetrahedral intermediates formed from alkoxide ions and trialkylboranes.[10] In these cases it has been proposed that the elimination reactions occur by stepwise mechanisms.



(**1**)



(**2**)



(**3**)

In this paper we explore both theoretically (using *ab initio* calculations) and experimentally (using both ion cyclotron resonance and flowing afterglow techniques) the course(s) of the reactions shown in (**1**), (**2**), and (**3**). We are interested in these reactions since they raise fundamental issues, *viz.* (*i*) is there equatorial–apical equilibration in a five-co-ordinate silicon intermediate, and (*ii*) is the elimination of the alkane a stepwise or concerted process?

Results and Discussion

Ion cyclotron resonance (i.c.r.) experiments were carried out using a Dynaspec ICR 9 spectrometer. Flowing afterglow experiments were performed at 300 K in a flowing afterglow (F.A.) system which has been described previously.[11] Summaries of both techniques are included in the Experimental section.

ab initio Calculations were carried out at the 6-21G level using GAUSSIAN 82.[12] We recognise that accurate representation of negatively charged species requires extended bases[13] preferably with a low exponent Gaussian in each set to

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† The term 1,2-elimination means that the groups being eliminated come from adjacent atoms. The term is not intended to imply a particular mechanism.

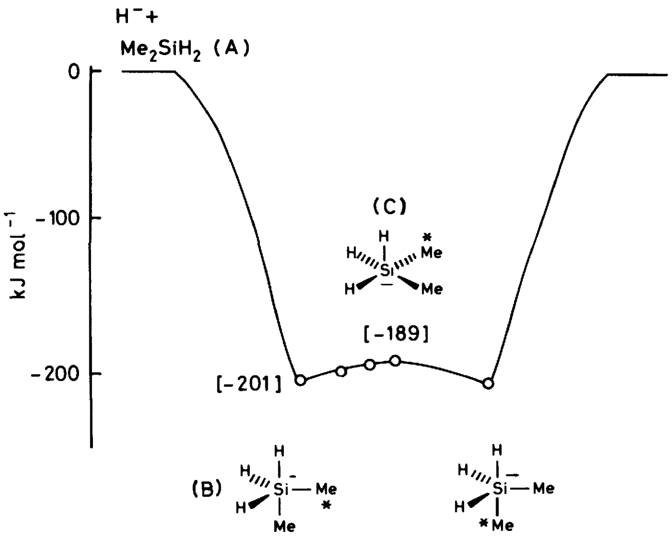


Figure 1. *ab initio* Calculations (6-21G) for the apical–equatorial conversion of substituents in $Me_2SiH_3^-$. Points shown are fully optimized in the direction of the reaction co-ordinate. Energies (a.u.) as follows: A, −369.18524, B, −369.66217, and C, −369.65764.

represent the diffuse outer region of negative ions. Nevertheless, we believe that systematic exploration (at a practical level) of the relative energies of intermediates and products is indispensible if complex reaction sequences are to be investigated. To support this view, we have shown that 4-31G and $6\text{-}311^{++}G$ calculations provide the same mechanistic information for the stepwise loss of molecular hydrogen from the ethoxide negative ion.[9] The procedures for exploring molecular system changes and for identifying overall reaction mechanisms have been described previously.[14],*

(A) *The Interchange of Apical and Equatorial Substituents.—ab initio* Calculations indicate that for attack of MeO^- on either silane or methylsilanes, the stable trigonal bipyramidal species in which a methoxy substituent occupies an apical position is only some 10 kJ mol^{-1} more negative in energy than that in which the MeO is in an equatorial position.[3,15] However, these five-co-ordinate structures are formed in the gas phase with energies of formation in the range[3,15] −200 to −300 kJ mol^{-1}. Provided this energy is not collisionally or radiatively dissipated, interchange of apical and equatorial substituents should occur. In Figure 1 we show the results of calculations on an exchange of apical and equatorial methyl groups in the model system $Me_2H_3Si^-$. We assume that the transition state for this thermoneutral reaction is the square pyramidal structure and we find that the barrier for the conversion is 12 kJ mol^{-1} at the 6-21G level. MNDO Calculations for similar exchanges of a variety of substituents indicate a barrier range[16] of 10—40 kJ mol^{-1}. From a theoretical viewpoint it may therefore be predicted that we will encounter equilibration of substituents in gas-phase reactions of five-co-ordinate silicon anions. It would however be difficult to devise an experiment to prove this prediction unequivocally.

(B) *The Reaction of Hydroxide Negative Ions with Tetramethylsilane.*—The prototypical 1,2-elimination reaction of an alkylsilane is the reaction between HO^- and tetramethylsilane [equation (1)]. The tetramethylsilane system is large for *ab initio* calculations, thus we have used $MeSiH_3$ as a model. We calculate the formation energy (at 6-21G) of intermediate $[Me(HO)H_3Si^-]$ to be −191 kJ mol^{-1} (with respect to reactants considered as 0 kJ mol^{-1}) and that the barrier for elimination of methane from this intermediate is 139 kJ mol^{-1}. The difference in energy between reactants and transition state is thus too large for entropic effects[17] to retard the reaction. The measured rate (F.A.) of 1.9×10^{-9} cm^3 $molecule^{-1}$ s^{-1} for reaction (1) is equal to the calculated ADO[18] rate: thus the reaction occurs at every collision.

$$HO^- + Me_4Si \longrightarrow Me_3SiO^- + CH_4 \tag{1}$$

$$HO^- + Me_3(CD_3)Si \longrightarrow$$

$$[Me_3(CD_3)(HO)Si^-] \longrightarrow Me_3SiO^- + CD_3H \tag{2}$$

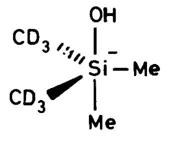
$$[Me_3(CD_3)(HO)Si^-] \longrightarrow Me_2(CD_3)SiO^- + CH_4 \tag{3}$$

$$HO^- + Me_2(CD_3)_2Si \longrightarrow$$

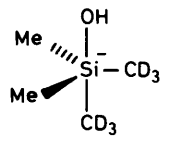
$$[Me_2(CD_3)_2(HO)Si^-] \longrightarrow Me_2(CD_3)SiO^- + CD_3H \tag{4}$$

$$[Me_2(CD_3)_2(HO)Si^-] \longrightarrow Me(CD_3)_2SiO^- + CH_4 \tag{5}$$

We have studied, in the flowing afterglow, the reactions of HO^- with both $Me_3(CD_3)Si$ and $Me_2(CD_3)_2Si$ to determine whether there is an isotope effect operating for the eliminations of variously labelled methanes. The reactions involved are (2)—(5). The relative counts (relative abundances) of product ions in the two reaction sequences are (2):(3) = 1:3, and (4):(5) = 1:1, *an exactly statistical elimination.* Two models may be used



(4)



(5)

to rationalize this behaviour, *viz.* (*i*) in the case of $Me_2(CD_3)_2Si$, if HO^- occupies an apical position, the two intermediates (**4**) and (**5**) should be formed equally, and in the absence of an isotope effect CH_4 and CD_3H should be lost in the ratio 1:1. If the HO^- occupies an equatorial position, a slightly more complex statistical analysis also indicates that CH_4 and CD_3H should be lost equally and (*ii*) equilibration of substituents [*cf.* section (A)] is occurring. We cannot differentiate experimentally between these possibilities. It is possible that both are correct.

(C) *The Reaction of Methoxide Ion with Tetramethylsilane.*— It is instructive to compare the results of flowing afterglow and

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* A referee has asked whether transition states represent saddle points on the potential-energy surfaces. We have discussed this matter in detail previously[14] and repeat it here. Plausible structures for transition states were identified as those of highest energy in a series of fully optimized supermolecules with fixed trial values of the significant reaction co-ordinate. We recognise that the choice of a single molecular co-ordinate as the reaction co-ordinate in a particular segment of reaction is essentially intuitive or conventional, and in principle an over-simplification. However, in our simple systems we believe the choice is reasonably obvious and realistic. We have not confirmed that our proposed transition-state geometries are true stationary states by full optimization to a single negative eigenvalue of the Hessian matrix, and instead regard these structures as merely plausible and as useful starting points for refinement should that be useful. A proposed transition state was always checked to see that it correctly led back to reactants and forward to relevant products by full relaxation after a small and appropriate distortion. All points in Figures 1—3 refer either to fully optimized reactant, product, or intermediate molecules, or to unstable species fully optimized at the indicated value of the stated molecular co-ordinate.

Table 1.

	Energy (a.u.)	Distances (Å)		Angles (°)	
MeO^-	−114.19956				
$MeSiH_3$	−330.17577				
(6)	−444.45101				
(7)	−444.37255	Si(1)–O(2)	1.666		
		O(2)–C(3)	1.456		
		H(4)–C(5)	2.867		
		C(5)–H(6)	3.619	O(2)–Si(1)–C(5)	71.81
		Si(1)–H(6)	1.482	C(5)–Si(1)–H(6)	45.50
		Si(1)–C(5)	4.50		
		Si(1)–H(7)	1.500		
(8)	−444.37788	Si(1)–O(2)	1.657	Si(1)–O(2)–C(3)	128.09
		O(2)–C(3)	1.484	O(2)–C(3)–H(4)	111.1
		C(3)–H(4)	1.076	C(3)–C(6)–H(7)	114.3
		C(3)–H(5)	1.072	C(3)–C(6)–H(8)	114.0
		C(3)–C(6)	3.05	O(2)–C(3)–H(5)	107.6
		H(5)–C(6)	2.84		
(9)	−444.36757	Si(1)–O(2)	1.645	Si(1)–O(2)–C(3)	130.05
		O(2)–C(3)	1.617	O(2)–C(3)–C(4)	178.85
		C(3)–C(4)	2.45		
(10)	−444.48182	O(1)–C(2)	2.62		
		O(1)–H(3)	2.83		
C_2H_6	−79.13802				
H_3SiO^-	−365.33661				
Me^-	−39.41215				
$MeOSiH_3$	−404.94109				

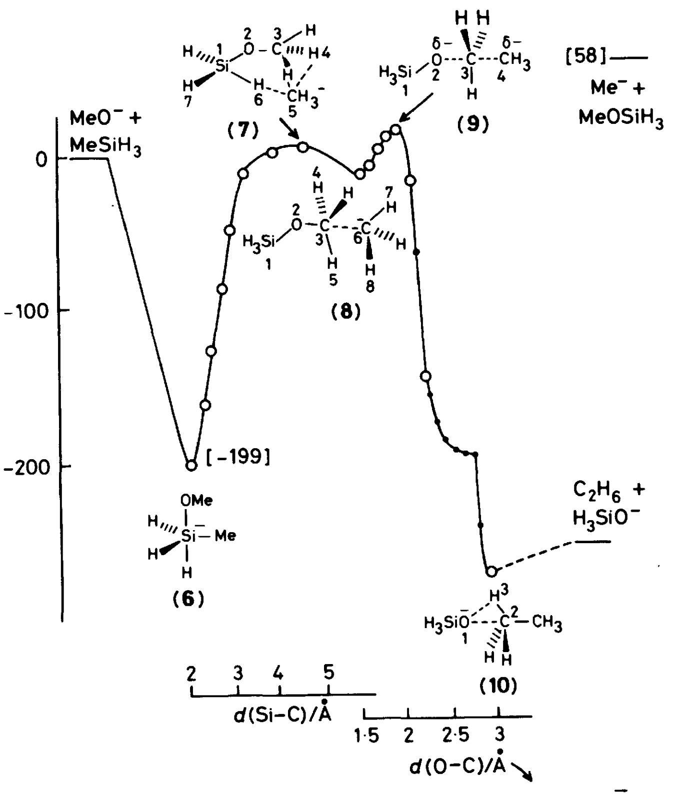

Figure 2. Results of *ab initio* calculations on the intermediates in the elimination of C_2H_6 from $Me(MeO)SiH_3^-$. Large points are fully optimized geometries in the direction of the appropriate reaction co-ordinate. Small points are derived from force-relaxation runs (potential-surface scans). For energies and geometries of species shown in Figure 2, see Table 1.

ion cyclotron resonance experiments for the MeO^-–Me_4Si system. I.c.r. shows the formation of a detectable adduct $[Me_4(MeO)Si^-]$ and the two reactions (6) and (7). Of the two elimination reactions (6) is the more pronounced.[3] Deuterium-labelling studies show that the groups eliminated are those shown in structure (**1**) and (**2**) respectively.[3] F.A. shows the formation of adduct $[Me_4(MeO)Si^-]$ and the elimination reaction (6). Reaction (7) is not observed. F.A. experiments are carried out in a helium buffer gas (at *ca.* 0.4 Torr) and so reactant ions will be of thermal energies. Reaction (7), observed in the i.c.r. experiment, is thus likely to come from excited MeO^- which in turn suggests that the energy barrier to this elimination is larger than the formation energy (excess of energy) of intermediate $[Me_4(MeO)Si^-]$. The rate of formation of the five-co-ordinate adduct is measured in the flowing afterglow as 1.4×10^{-9} cm^3 molecule^{-1} s^{-1} (calculated ADO[18] rate: 1.5×10^{-9} cm^3 molecule^{-1} s^{-1}); thus adduct formation occurs at every collision. In contrast, the experimental (F.A.) rate of reaction (6) is 1.0×10^{-10} cm^3 molecule^{-1} s^{-1}, which means that on average *ca.* 7% of the initial five-co-ordinate intermediates have sufficient energy to eliminate ethane. Thus the energetic requirements for reactions (6) and (7) are quite different from that of reaction (1), described above.

$$\mathrm{MeO^- + Me_4Si} \longrightarrow$$
$$[\mathrm{Me_4(MeO)Si^-}] \begin{array}{ll} \nearrow \mathrm{Me_3SiO^- + C_2H_6} & (6) \\ \searrow \mathrm{Me_2(MeO)SiCH_2^- + CH_4} & (7) \end{array}$$

We now describe *ab initio* calculations (at the 6-21G level) of the model reaction systems: (*i*) the intermediate $[MeH_3(MeO)Si^-]$ eliminating ethane and (*ii*) the intermediate $[Me_2H_2(MeO)Si^-]$ eliminating methane. The reaction paths ascending towards barriers were searched as a series of fully relaxed geometries about a selected and fixed molecular co-ordinate, for example the length of a breaking bond. Descending paths were searched by total relaxation of geometry down to the next potential minimum.

The results for the elimination of ethane from [$MeH_3(MeO)Si^-$] are summarized in Figure 2.* Since five-co-ordinate adducts are formed with excess of energy, interchange of substituents on silicon will certainly occur [*cf.* Section (A), in particular Figure 1]. For computational convenience we have taken (**6**) (Figure 2) as the decomposing intermediate and placed the methoxy group in the preferred apical position. We have assumed that the first step in the decomposition of (**6**) is the breaking of the Si–C bond and find that the departing Me^- needs to withdraw 3.5 Å before the system relaxes to the intermediate (**8**), the precursor of ethane elimination. The reaction proceeds through the association complex (**10**) which in turn dissociates to H_3SiO^- and ethane. Although the overall reaction is exothermic [-261 kJ mol^{-1} (6-21G)], the barrier is high and marginally endothermic. The calculation thus indicates that if this reaction does occur, then it will certainly be slow.† Reaction (6) is slow: its mechanism should be very similar to that shown in Figure 2.

The results obtained for the loss of methane from [$Me_2H_2(MeO)Si^-$] are summarized in Figure 3. The approach of MeO^- to yield the five-co-ordinate adduct (**11**) and subsequent departure of Me^- must follow paths very similar to those described above for the MeO^-–$MeSiH_3$ system (Figure 2), and these have not been calculated in detail. It is interesting that at 6-21G, (**12**) relaxes without interception of barriers to associated products (**14**). This is a different result to that obtained for the analogous region of Figure 2. Unfortunately, this system is too large for us to undertake calculations at the $6\text{-}31^{++}G$ level. We have thus carried out supplementary calculations relevant to the appropriate region of Figure 3 at the $6\text{-}31^{++}G$ level for the model system Me^-–$MeSiH_3$, where Me^- interacts with the methyl group of methylsilane. From these studies we infer the system relaxes to a weak solvated methyl ion complex [detected at 6-21G as (**13**), Figure 3] and that this complex is transformed to (**14**) by passing over a barrier whose crest lies some 20 kJ mol^{-1} above that of the reactants. *This pathway is not detected at the* 6-21G *level.* In any event, we believe that the solvated methyl anion [in the vicinity of (**12**) to (**13**), Figure 3] should be considered as an orbiting complex, with the methyl anion orbiting the silicon moiety and keeping in random contact with methoxy and methyl substituents. The orbiting complex is an effective entropy bottleneck in the reaction since (*i*) it has many degrees of internal freedom and (*ii*) dissociation to Me^- and the methoxysilane is endothermic ($+45$ kJ mol^{-1}; Figure 3). Overall, the loss of methane depicted in Figure 3 should be a slow reaction, because of the considerable internal barrier.‡

Finally, we have studied, using ion cyclotron resonance, the deuterium isotope effects observed for reactions (6) and (7). In the prototypical elimination (1) no deuterium isotope effect is observed because the decomposing intermediate [$Me_4(HO)Si^-$] has considerably more energy than is required to surmount the barrier and form the products Me_3SiO^- and CH_4. In contrast, the energy barriers for reactions (6) and (7) are large and deuterium isotope effects would be expected. The ratios of the observed losses of labelled and unlabelled ethanes and methanes in the i.c.r. reactions of MeO^- and CD_3O^- with $Me_2(CD_3)_2Si$ are listed in Table 2.

Table 2. Losses of (labelled) ethane and methane from the reactions of MeO^- and CD_3O^- with $Me_2(CD_3)_2Si$ (i.c.r.)

System	Loss and ratio CH_4:CH_3D:CD_3H:CD_4			
MeO^-–$Me_2(CD_3)_2Si$	40	20	40	*a*
CD_3O^-–$Me_2(CD_3)_2Si$	35	25	40	*a*
MeO^-–$Me_2(CD_3)_2Si$	MeMe:$MeCD_3$ = 60:40			
CD_3O^-–$Me_2(CD_3)_2Si$	$MeCD_3$:CD_3CD_3 = 52:48			

[a] The loss of CD_4 is not observed, but an elimination comprising *ca.* 5% would certainly be lost in baseline noise [the loss of CH_4 in the reaction between MeO^- and Me_4Si is quite small, the product ion is only 8% of the main peak (MeO^-, 100%)].[3]

The small isotope effect observed for the various eliminations of ethane reflects the presence of a secondary isotope effect in the first step of the elimination [*cf.* (**6**) $\longrightarrow$ (**8**), Figure 2]. It is likely that the second step of this reaction [*cf.* (**8**) $\longrightarrow$ (**10**)] is also kinetically significant,[8,9] but we cannot of course measure an isotope effect for this step. No isotope effect should be apparent for the final step [*cf.* (**10**) $\longrightarrow$ H_3SiO^- (Figure 2)] since the last formed intermediate is highly energetic.

The various losses of methane provide a more interesting scenario. We do not have *ab initio* results for the system MeO^-–Me_4Si and we are using Figure 3 as a model. The reaction (**11**) to (**14**) is certainly not synchronous since an Si–C bond is broken for (**11**) to (**12**), whereas from (**12**) to (**14**) one C–H bond is breaking while a second is forming. Let us therefore calculate isotope effects from the ratios given in Table 2, assuming (*i*) that the isotope effects associated with the cleavage of the Si–C bond and the formation of the C $\cdots$ H–C unit can be calculated separately and (*ii*) that equilibration of Me and CD_3 substituents occurs in initial intermediates [$Me_2(CD_3)_2(RO)Si^-$] (R = Me or CD_3; see Table 2). A secondary isotope effect of 1.25 for Si–C bond cleavage and a primary isotope effect of 3.0 for formation of C $\cdots$ H–C gives a loss ratio CH_4:CH_3D:CD_3H:CH_4 of 32:25:37:7. Such values are not inconsistent with the proposed mechanism.

Conclusions

In this study we have attempted to answer the questions posed in the introduction. In summary (*i*) there is theoretical evidence to suggest that equilibration of apical and equatorial sub-

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* Supplementary calculations (at the $6\text{—}31^{++}G$ level) on the approach of small negative ions (H^-, F^- and HO^-) from a variety of directions towards a methyl group of $MeSiH_3$, establish that there are no significant association complexes of the type $X^- \cdots H_3CSiH_3$. The minimum-energy path of CH_3O^- approaching a methyl group is one that skirts around the van der Waals envelope of the methyl group (at an $O^- \cdots C$ radius of *ca.* 3.0 Å) to enter the steepening channel to the silicon centre and to form a five-co-ordinate adduct. Deprotonation complexes of the type $XH \cdots {}^-CH_2SiH_3$ do exist but they are reached by a departure from the main channel after surmounting a barrier of some 30 kJ mol^{-1}.

† The reaction we are using as model for the process $MeO^- + Me_4Si \longrightarrow Me_3SiO^- + C_2H_6$ does occur as a minor process in the MeO^-–$MeSiH_3$ system. An F.A. study of the CD_3O^-–$MeSiH_3$ system shows the following processes (branching ratios in parentheses):

$$CD_3O^- + MeSiH_3 \longrightarrow Me(CD_3O)H_3Si^- \ (0.41)$$
$$CD_3O^- + MeSiH_3 \longrightarrow MeH_2SiO^- + CD_3H \ (0.57)$$
$$CD_3O^- + MeSiH_3 \longrightarrow H_3SiO^- + MeCD_3 \ (0.02)$$

‡ As noted above, the process $MeO^- + Me_4Si \longrightarrow Me_2(MeO)SiCH_2^- + CH_4$ is *not* observed in the F.A. In contrast, the model reaction described in Figure 3 is observed but in small yield. An F.A. study of the CD_3O^-–Me_2SiH_2 system shows the following processes (branching ratios in parentheses):

$$CD_3O^- + Me_2SiH_2 \longrightarrow Me_2(CD_3O)H_2Si^- \ (0.48)$$
$$CD_3O^- + Me_2SiH_2 \longrightarrow Me_2HSiO^- + CD_3H \ (0.42)$$
$$CD_3O^- + Me_2SiH_2 \longrightarrow (CD_3O)H_2SiCH_2^- + CH_4 \ (0.05)$$
$$CD_3O^- + Me_2SiH_2 \longrightarrow MeH_2SiO^- + MeCD_3 \ (0.04)$$

Table 3.

	Energy (a.u.)	Distances (Å)		Angles (°)	
MeO^-	−114.19956				
Me_2SiH_2	−369.18524				
(11)	−483.45605				
(12)	−483.38116	Si(1)–H(2)	1.52		
		Si(1)–O(3)	1.72		
		O(3)–C(4)	1.472	C(7)–Si(1)–C(5)	48.3
		C(5)–H(6)	1.462	H(6)–C(7)–H(10)	126.2
		H(6)–C(7)	1.436	O(3)–Si(1)–C(7)	68.3
		C(7)–H(8)	1.101	Si(1)–C(7)–H(8)	55.1
		C(7)–H(9)	1.093		
		C(7)–H(10)	1.093		
		Si(1)–C(7)	3.50		
(13)	−483.38542	Si(1)–H(2)	1.51		
		Si(1)–O(3)	1.70		
		O(3)–C(4)	1.42	O(3)–Si(1)–C(5)	115.7
		C(5)–H(6)	1.10	Si(1)–C(7)–H(8)	105.8
		H(6)–C(7)	2.61	Si(1)–O(3)–C(4)	126.5
		C(7)–H(8)	1.11		
		C(7)–H(9)	1.11		
		Si(1)–C(7)	4.50		
(14)	−483.44432	Si(1)–H(2)	1.529		
		Si(1)–O(3)	1.743		
		O(3)–C(4)	1.415		
		Si(1)–C(5)	1.771	Si(1)–C(5)–H(6)	122.0
		C(5)–H(6)	1.079	C(5)–H(6)–H(7)	199.3
		C(5)–H(7)	2.897		
		H(7)–C(8)	1.084		
		C(8)–H(9)	1.085		
CH_4	−40.14926				
$H_2(MeO)SiCH_2^-$	−443.29008				
Me^-	−39.41215				
$Me(MeO)SiH_2$	−443.95560				

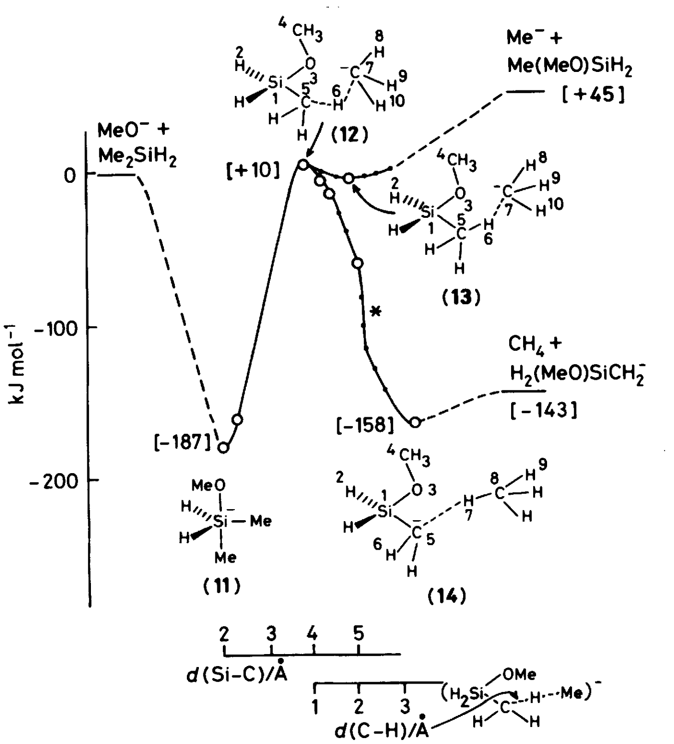

Figure 3. Results of *ab initio* calculations on the intermediates in the elimination of CH_4 from $Me_2(MeO)SiH_2^-$. Large points are fully optimized geometries in the direction of the appropriate reaction co-ordinate. Small points are derived from force-relaxation runs (potential-surface scans). For energies and geometries of species shown in Figure 3, see Table 3. * In this region there is a rapid shortening of the H–C bond.

stituents may occur in energized trigonal bipyramidal silicon negative ions in the gas phase and (*ii*) *ab initio* calculations of model systems indicate that the 1,2-elimination reactions which occur in the MeO^-–Me_4Si system are stepwise with large internal barriers. Deuterium isotope effects are observed for these reactions.

Experimental

I.c.r. spectra were measured with a Dynaspec ICR 9 spectrometer equipped with a three-section cell, operating at 70 eV (primary negative ions formed by dissociative secondary electron capture), and using an ion transit time of 1×10^{-3} s. Other reaction conditions, $\omega_c/2\pi$ 153.7 kHz, RONO pressure 5×10^{-6} Torr, pressure of substrate 1×10^{-5} Torr. The total ion current was in the 10^{-10} A range, emission current 0.2 μA. Ratios of product ions given in Table 2 are an average of ten separate measurements.

Alkoxide negative ions were formed in the i.c.r. cell with either MeONO or CD_3ONO prepared[19] on the day of the experiment. Tetramethylsilane was a commercial sample. $Me_3(CD_3)Si$ and $Me_2(CD_3)_2Si$ were prepared by reported procedures[20] ($^2H_3$ = 99% and $^2H_6$ = 99% respectively).

Flowing afterglow experiments were carried out at 300 K in a system described previously.[11] In summary, the system consists of a 100 cm × 7 cm i.d. flow reactor affixed to a quadrupole mass spectrometer. A fast flow (80 m s^{-1}) and relatively high pressure (0.4 Torr) of helium buffer gas is maintained in the flow tube by a Roots blower. The HO^- ion was generated from N_2O (1 μ) and CH_4 (2 μ). The MeO^- ion was generated from $MeOCH_2CH_2OMe$ by reaction with NH_2^- (produced by electron bombardment of ammonia).[21] CD_3O^- was similarly generated from $CD_3OCD_2CD_2OCD_3$. The neutral species to be treated with either HO^- or MeO^- is introduced into the system through the moveable inlet placed at least 10 cm downstream of the area of HO^- (or MeO^-) generation. Flow rates were determined by monitoring the pressure of substrate increase with time in a calibrated volume. Rate coefficients were measured by following reactant ion counts as a function of time. Measurements were made at several neutral flow rates, and reported values are an average of these measurements. The experimental precision of each rate constant is better than ±10%: the overall accuracy is estimated to be ±25%. Branching ratios were measured as described previously.[22] ADO rates were calculated by the method of Su and Bowers[18] and can be considered to be correct to ±20%.

All neutral reagents used in the F.A. experiments were obtained from commercial sources. Gases were of the following purities: He (99.997%), NH_3 (99.999%), N_2O (99.99%), and CH_4 (99.99%).

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