Rearrangement *vs.* Dissociation of Gaseous Silicon-containing Cations: a Combined Experimental–Theoretical Approach

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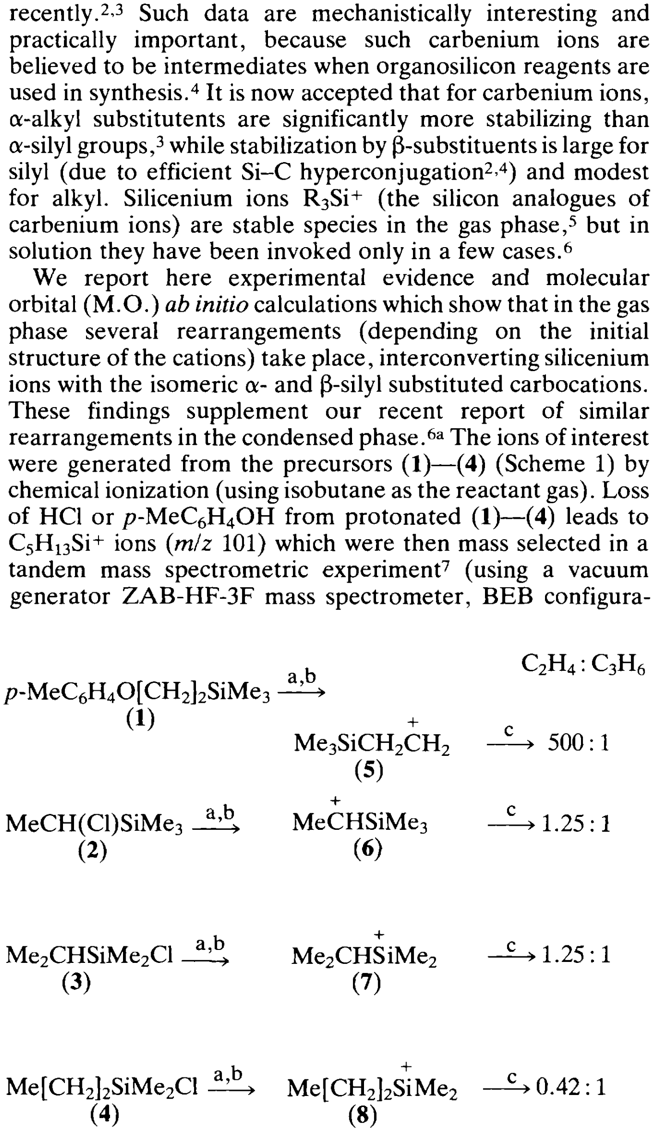
The dissociative ionizations of p-$MeC_6H_4O[CH_2]_2SiMe_3$, $MeCH(Cl)SiMe_3$, $Me_2CHSiMe_2Cl$, and $Me[CH_2]_2SiMe_2Cl$ were studied in the gas phase, experimentally by using tandem mass spectrometric techniques (MS/MS) and computationally by *ab initio* M.O. methods, revealing a complex scheme of rearrangements that interconvert the resulting isomeric $C_5H_{13}Si^+$ ions, including silicenium ions and α- and β-silyl substituted carbocations.

There is considerable current interest in organosilicon chemistry,[1] but many basic questions such as the stabilities of α- and β-silyl substituted carbenium ions have been evaluated only recently.[2,3] Such data are mechanistically interesting and practically important, because such carbenium ions are believed to be intermediates when organosilicon reagents are used in synthesis.[4] It is now accepted that for carbenium ions, α-alkyl substitutents are significantly more stabilizing than α-silyl groups,[3] while stabilization by β-substituents is large for silyl (due to efficient Si–C hyperconjugation[2,4]) and modest for alkyl. Silicenium ions R_3Si^+ (the silicon analogues of carbenium ions) are stable species in the gas phase,[5] but in solution they have been invoked only in a few cases.[6]

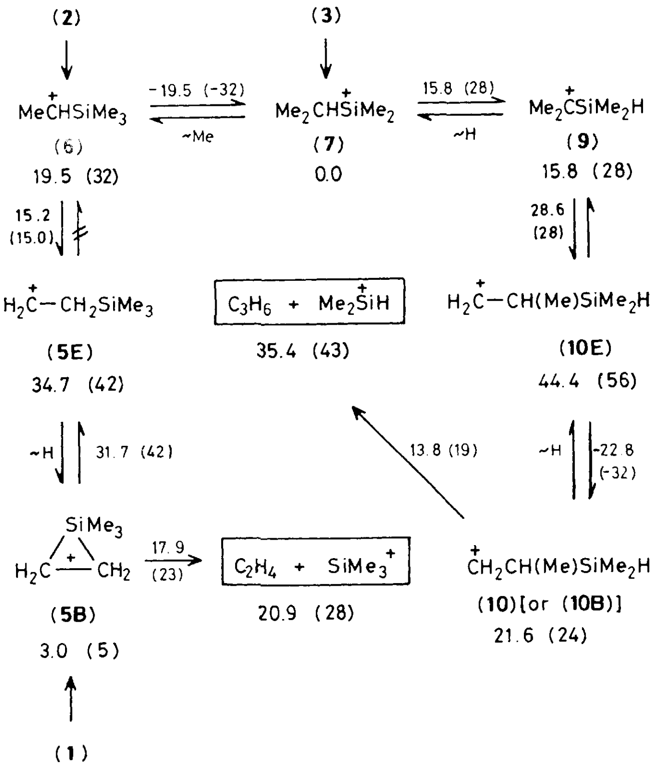
We report here experimental evidence and molecular orbital (M.O.) *ab initio* calculations which show that in the gas phase several rearrangements (depending on the initial structure of the cations) take place, interconverting silicenium ions with the isomeric α- and β-silyl substituted carbocations. These findings supplement our recent report of similar rearrangements in the condensed phase.[6a] The ions of interest were generated from the precursors (**1**)—(**4**) (Scheme 1) by chemical ionization (using isobutane as the reactant gas). Loss of HCl or p-MeC_6H_4OH from protonated (**1**)—(**4**) leads to $C_5H_{13}Si^+$ ions (*m/z* 101) which were then mass selected in a tandem mass spectrometric experiment[7] (using a vacuum generator ZAB-HF-3F mass spectrometer, BEB configuration with *B* magnetic and *E* electric field), and subjected to collision induced dissociations[8] occurring in the 3rd field-free region of the instrument. The resulting mass spectra did not contain signals originating from unimolecular dissociations which can be affected by internal energy effects.[8] Thus, the spectra reflect directly the structural characteristics of the generated $C_5H_{13}Si^+$ ions.

Insight into the processes in Scheme 1 is provided by *ab initio* M.O. calculations[9] for relevant intermediates and transition structures on the $C_5H_{13}Si^+$ potential energy surface (p.e.s.), shown in Schemes 2 and 3. Geometries were generally optimized with the 3–21G basis set[10a] and single point calculations at 6–31G* [10b] followed. The calculated relative energies, at the 6–31G*//3–21G level are also given in Schemes 2 and 3. We also calculated, at higher levels of theory (up to MP2/6–31G*//6–31G*[10c]), the smaller cations $MeCH_2SiH_2^+$, $Me(SiH_3)CH^+$, and the open and silyl-bridged $H_3SiCH_2CH_2^+$ (for similar calculations see ref. 2a). The latter

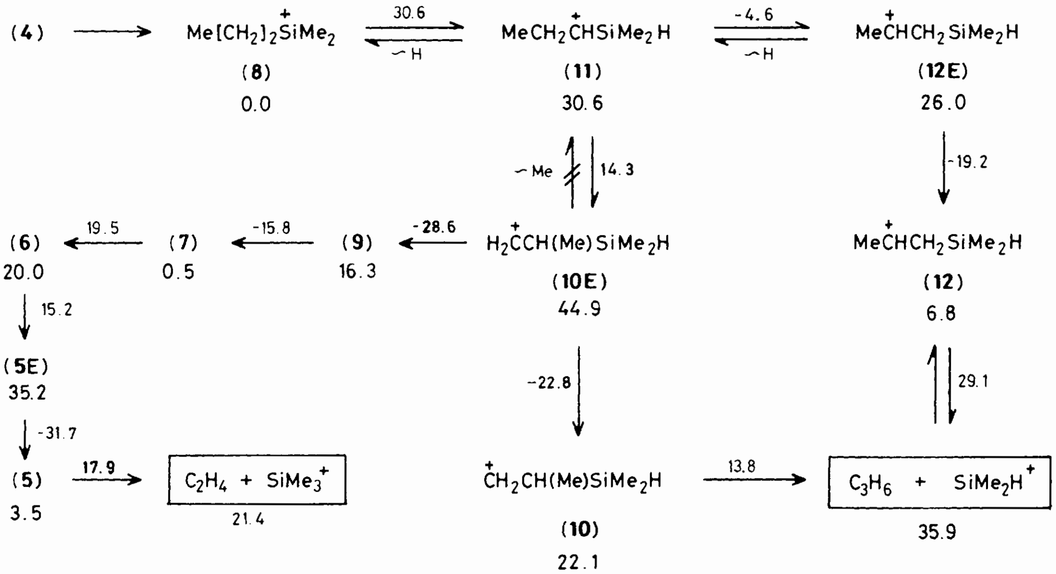


$$\text{C}_2\text{H}_4:\text{C}_3\text{H}_6$$
$$\underset{(\mathbf{1})}{p\text{-MeC}_6\text{H}_4\text{O[CH}_2]_2\text{SiMe}_3} \xrightarrow{a,b} \underset{(\mathbf{5})}{\text{Me}_3\text{SiCH}_2\overset{+}{\text{C}}\text{H}_2} \xrightarrow{c} 500:1$$
$$\underset{(\mathbf{2})}{\text{MeCH(Cl)SiMe}_3} \xrightarrow{a,b} \underset{(\mathbf{6})}{\text{Me}\overset{+}{\text{C}}\text{HSiMe}_3} \xrightarrow{c} 1.25:1$$
$$\underset{(\mathbf{3})}{\text{Me}_2\text{CHSiMe}_2\text{Cl}} \xrightarrow{a,b} \underset{(\mathbf{7})}{\text{Me}_2\text{CH}\overset{+}{\text{Si}}\text{Me}_2} \xrightarrow{c} 1.25:1$$
$$\underset{(\mathbf{4})}{\text{Me[CH}_2]_2\text{SiMe}_2\text{Cl}} \xrightarrow{a,b} \underset{(\mathbf{8})}{\text{Me[CH}_2]_2\overset{+}{\text{Si}}\text{Me}_2} \xrightarrow{c} 0.42:1$$

Scheme 1. a, Gas phase protonation with $C_4H_9^+$; b, loss of p-MeC_6H_4OH from protonated (**1**) and HCl from protonated (**2**), (**3**), and (**4**); c, collisional activation resulting in the elimination of C_2H_4 and C_3H_6, corresponding to the formation in the given ratios of $SiMe_3^+$ (*m/z* 73) and HMe_2Si^+ (*m/z* 59), respectively. These ions correspond to more than 98% of the total ion current of the collision induced fragments.



Scheme 2. Calculated relative energies (kcal/mol; 1 kcal = 4.184 kJ) at 6–31G*//3–21G. Values in parentheses are 'corrected' energies (see text). The total 6–31G*//3–21G energy of (**7**) is −485.59157 hartrees.



Scheme 3. Calculated relative energies (kcal/mol) at 6–31G*//3–21G. The total energy of (**8**) at this level is −485.59240 hartrees.

calculations allow us to correct for deficiencies of the less sophisticated theoretical methods that had to be applied for the larger $C_5H_{13}Si^+$ cations. The 'corrected' values which were obtained using this information (see below) are given in parentheses in Scheme 2.

At MP2/6–31G*//3–21G (MP2/6–31G*//6–31G* gives similar results). $MeCH_2SiH_2^+$ is the relevant most stable $C_2H_7Si^+$ species, but the silyl-bridged $H_3SiCH_2CH_2^+$ is only 5.5 kcal/mol higher in energy ('open' $H_3SiCH_2CH_2^+$ is not a minimum on the p.e.s., in agreement with labelling experiments[11]). $Me(SiH_3)CH^+$ lies much higher in energy than $MeCH_2SiH_2^+$, *i.e.*, by 31.0 kcal/mol, and it is probably not a stationary point on the $C_2H_7Si^+$ p.e.s. Thus, at MP2/6–31G*, 1,2-H shifts either to $EtSiH_2^+$ or to the silyl-bridged $H_3Si[CH_2]_2^+$ occur spontaneously.[12] This stability order remains qualitatively the same in the related trimethyl-substituted $C_5H_{13}Si^+$ cations. At 6–31G* the relative energies of (**7**), (**5B**), and (**6**) are: 0, 3.0, and 19.5 kcal/mol, respectively. Based on the relative energies at 6–31G* and MP2/6–31G* of the $C_2H_7Si^+$ cations, we estimate (*i.e.*, 'corrected' value) that at MP2/6–31G* the relative energies of (**7**), (**5B**), and (**6**) are *ca.* 0, 5, and 32 kcal/mol, respectively. Furthermore, in (**6**) (and other similar high energy cations) the barriers for exothermic 1,2-H shifts [*e.g.*, (**11**) → (**8**)] are tiny (or vanish), and those for 1,2-methyl shifts [*e.g.*, (**6**) → (**7**)] are at most a few kcal/mol.[12] On the basis of these calculations we now analyse the experimental results.

Starting with (**1**), (**5B**) is first generated. The rearrangement to (**6**) *via* (**5E**) requires 32 kcal/mol (42 kcal/mol, 'corrected'), a much higher energy than the dissociation energy of (**5**) to ethylene and Me_3Si^+ (17.9 kcal/mol at 6–31G*, 23 kcal/mol 'corrected'). In agreement with this, dissociation is the only observed process for (**1**).

A more demanding challenge is to explain the identical product mixtures obtained from (**2**) and (**3**). Dissociation of ($3^{+\bullet}$) yields (**7**), a local minimum on the $C_5H_{13}Si^+$ p.e.s. Rearrangements of (**7**), either *via* (**7**) → (**6**) → (**5**) → [C_2H_4 + Me_3Si^+], or *via* (**7**) → (**9**) → (**10**) → [C_3H_6 + Me_2SiH^+] are endothermic, but far less than its direct fragmentation {*e.g.*, (**7**) → [$Me_2CH^\bullet$ + $Me_2Si^{+\bullet}$], requiring 135 kcal/mol at 6–31G*//3–21G}. Thus, in contrast to (**5B**), (**7**) rearranges prior to fragmentation. With precursor (**2**) one enters the p.e.s. close to (**6**), which is 32 kcal/mol ('corrected') higher in energy than (**7**). The fact that (**6**) is a minimum on the p.e.s. is probably an artefact of the 3–21G basis set.[12] In reality (**6**) is expected to rearrange to (**7**) spontaneously (or with a small barrier). The rearrangement of (**6**) to (**5B**) is also highly exothermic but a significant barrier of 15.2 kcal/mol separates these species. This barrier results from the fact that a 1,2-H shift in (**6**) produces the eclipsed conformation (**5E**) (*i.e.*, HC^+CSi = 0°), which is 32 kcal/mol higher in energy than conformation (**5**). In (**5**), but not in (**5E**), the empty 2p (C^+) orbital and the C–Si bond are in the same plane, forming a favourable stereochemistry for the hyperconjugative stabilization of the cation and for its fragmentation to C_2H_4 and Me_3Si^+ (Figure 1). Thus, the calculations predict that (**2**) and (**3**) dissociate to a common intermediate (**7**). This conclusion is in complete agreement with the observation that (**2**) and (**3**) yield identical product mixtures (Scheme 1).

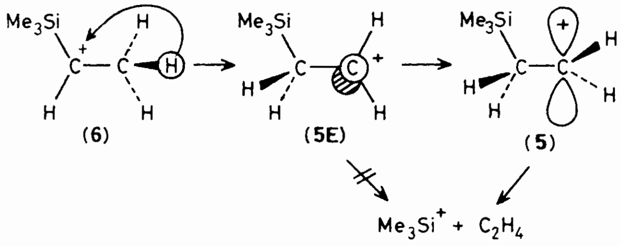


Figure 1

What is the fate of (**7**)? The fragmentation products of (**7**) are not thermodynamically controlled. The energy of [C_2H_4 + Me_3Si^+] is lower by 14.5 kcal/mol than that of [C_3H_6 + Me_2SiH^+],† but experimentally these fragments are obtained in a ratio close to 1:1. The calculated barriers for these

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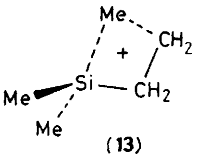
† Using the experimental data from the references given below we calculate that this energy difference is 14.4. kcal/mol (J. R. Krause and P. Potzinger, *Int. J. Mass Spectrom. Ion Phys.*, 1975, **18**, 303), and 20.0 kcal/mol (G. W. Goodloe, E. R. Austin, and F. W. Lampe, *J. Am. Chem. Soc.*, 1979, **101**, 3472), in good agreement with the calculations.



(13)

fragmentation processes are 34.7 kcal/mol (42 kcal/mol, 'corrected') for (**7**) → [C_2H_4 + Me_3Si^+] [highest point (**5E**)] and 44.4 kcal/mol (56 kcal/mol, 'corrected') for (**7**) → [C_3H_6 + Me_2SiH^+] [highest point (**10E**)], suggesting that fragmentation to [C_2H_4 + Me_3Si^+] should be favoured kinetically. This prediction is inconsistent with experimental results. The discrepancy may result from the fact that the rates of the processes which determine the product distribution are governed by entropy, not by enthalpy. While for most long-lived ions enthalpy seems to be dominant,[13] cases are known (for gaseous anions[14] and cations[15]), in which the reaction having the higher activation energy proceeds faster, and *vice versa*.

Protonation of (**4**) followed by loss of HCl produces (**8**), which is the global minimum on the $C_5H_{13}Si^+$ p.e.s. According to calculations (Scheme 3), the lowest energy path available to (**8**) is (**8**) → (**11**) → (**12E**) → (**12**) ('open' or 'bridged') → [C_3H_6 + $SiMe_2H^+$]; (**11**) having the highest energy. This predicted pathway is in agreement with experimental results; starting with (**4**), the major ion observed is Me_2HSi^+.

However, substantial dissociation of (**4**) to [C_2H_4 + Me_3Si^+] also occurs. A possible reaction path leading to Me_3Si^+ is (**4**) → (**8**) → (**11**) → (**10E**) → (**9**) → (**7**) → (**6**) → (**5E**) → (**5**) → [C_2H_4 + Me_3Si^+]. (**10E**), the highest point along this path, is 44.9 kcal/mol above (**8**) and 14.3 kcal/mol above (**11**). The fact that significant fragmentation to [C_2H_4 + Me_3Si^+] does occur (Scheme 1) may indicate that relative to (**11**) the calculated energy of (**10E**) is too high, or that factors which are not included in the calculations (such as entropy and density of states) contribute significantly. Other reaction paths which we examined are even higher in energy; *e.g.*, (**13**), the transition state for the direct rearrangement of (**8**) to (**5**), lies 16.8 kcal/mol above (**10E**).

We are studying similar rearrangements in related systems, such as 2-trimethylsilyl-2-adamantyl chloride,[6a] both in the gas phase and in solution.‡

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‡ We draw attention here to two related papers. (a) K. Hoffmann, *J. Prakt. Chem.*, 1981, **323**, 399, reported that Et_2SiD^+ eliminates C_2H_4 and C_2H_3D in a 2 : 1 ratio; this observation also requires that prior to dissociation, Et_2SiH^+ undergoes reversible rearrangement. The exchange reaction does not involve the molecular ions $Et_3SiD^{+\cdot}$, as the latter eliminates specifically $C_2H_5^{\cdot}$. (b) T. M. Mayer and F. W. Lampe, *J. Phys. Chem.*, 1974, **78**, 2433, invoked rearrangements involving silicenium ions and silyl-substituted carbenium ions to account for the observation of Et_3Si^+ in the gas phase ion–molecule reactions of SiH_3^+ and C_2H_4.