Experimental Evidence for Novel Hydrogen/Methyl Exchange Processes Preceding the Unimolecular Dissociation of Silicon-Containing Cations in the Gas Phase[†]

Thomas Drewello,[‡,§] Peter C. Burgers,[∥] Waltraud Zummack,[‡] Yitzhak Apeloig,[⊥] and Helmut Schwarz[*,‡]

Institut für Organische Chemie, Technische Universität Berlin, D-1000 Berlin 12, FRG, Department of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel, and Institute of Mass Spectrometry, University of Amsterdam, NL-1018 WS Amsterdam, The Netherlands

Isotopic labeling is used to demonstrate that the "nascent" α-silyl-substituted carbenium ion $CH_3C^+(H)Si(CH_3)_3$ prior to dissociation to C_2H_4 and $Si(CH_3)_3{}^+$ rapidly undergoes 1,2-methyl migrations leading to an almost complete exchange of the four methyl groups. The ion also undergoes slow 1,2-hydrogen shifts with a kinetic isotope effect k_H/k_D of approximately 2.5. These results are in good agreement with previous ab initio molecular orbital (MO) calculations. The tertiary silyl-substituted carbenium ion $(CH_3)_2C^+Si(CH_3)_3$ also exchanges, prior to loss of propene, its five methyl groups in a nearly quantitative way. Loss of propene immediately follows upon a rate-determining 1,2-hydrogen shift which has a kinetic isotope effect of 2.5. The unimolecular chemistry of the two homologous ions thus appears remarkably similar.

Introduction

Organosilicon compounds play an increasingly important role in materials science as well as synthetic, analytical, and physical organic chemistry,[1] and the rich chemistry of silicon-containing ions in the gas phase forms a subject of current interest.[2] This is partly due to the fact that, on one hand, silyl substituents exert pronounced effects on the stability of carbocations and, to a smaller extent, of carbanions as well. In addition, there is increasing experimental evidence that the gas-phase cation chemistry of organosilicon compounds including silicenium ions and α- and β-silyl-substituted carbocations is quite complex in that a number of interesting rearrangements occur.[2a,c,3] Such rearrangements have been observed also in the condensed phase, resulting in the first solvolytic generation of a silicenium ion.[4] The operation of (reversible) rearrangement processes is, for example, indicated by the following observations:

(1) The deuterated silicenium ion $(CH_3CH_2)_2SiD^+$ eliminates in the gas phase C_2H_4 and C_2H_3D in a 2:1 ratio, which is, if one takes into account the operation of kinetic isotope effects, close to the statistical value of 1.5:1 calculated for an equilibration of the four methylene hydrogens and the deuterium atom.[5]

(2) The formation of $(C_2H_5)_3Si^+$ ions in the gas-phase ion/molecule reactions of $SiH_3{}^+$ and C_2H_4 implies the intermediacy of silicenium ions and silyl-substituted carbocations,[6] and the observation that in the reactions of $SiH_3{}^+$ and C_2D_4 inter alia $SiH_{3-x}D_x{}^+$ ($x = 0$–3) ions are observed points to the existence of long-lived collision complexes that are capable of undergoing reversible H/D exchange.[7]

(3) Facile hydrogen- and methyl-exchange processes were recently reported for the reactions of $SiH_x(CH_3)_{3-x}{}^+$ ($x = 1$–3) and propene in gas phase.[8] Quite remarkable, in this study,[8] are the following facts, all of which point

to formation of species earlier suggested by Apeloig et al.[3a] in a combined theoretical/experimental study: (i) C_2D_4 yields exclusively *one* H/D exchange with $Si(CH_3)_2H^+$ to generate $Si(CH_3)_2D^+$. The methyl groups of the silicenium ion are not involved in the exchange process as evidenced by the finding that no deuterium incorporation is observed for the reactions of C_2D_4 with either $Si(CH_3)_2D^+$ or $Si(CH_3)_3{}^+$. (ii) In the reactions of $Si(CH_3)_2D^+$ with CH_3C—CH_2 and of $Si(CH_3)_2H^+$ with CH_3CD—CH_2, strikingly similar isotopic product distributions are observed. Of particular interest is the fraction of symmetric H/D exchange product (18 versus 16%). In contrast, the reaction of $Si(CH_3)_2H^+$ with CD_3CH—CH_2 yields only 1% of single H/D exchange.

While these and many other[2a,c] findings are in line with a high propensity of Si-containing species to rearrange, there is also compelling evidence that some of the cations must reside in deep potential wells, preventing them to undergo facile interconversion.[2a,c,3] This is, for example, indicated by (i) the distinct collisional activation (CA)[9] mass spectra,[3a] (ii) the different ion/molecule reactivity,[3b] and (iii) absence of H/D scrambling in some cationic Si-containing isomers.[2a,c] A few examples may suffice to illustrate this point: Collisional activation of the $C_2D_4/Si(CH_3)_3{}^+$ adduct ion results in loss of only C_2D_4.[3b] In biomolecular reactions of the $C_2H_4/Si(CH_3)_3{}^+$ adduct ion with σ- or π-donor Lewis bases, the major process corresponds to the exclusive displacement of ethylene by the

---

(1) For an excellent overview including experimental and theoretical aspects, see: *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989.

(2) For recent reviews, see: (a) Oppenstein, A.; Lampe, F. W. *Review of Chemical Intermediates*; Strausz, O. P., Ed.; Elsevier: Amsterdam, 1986; Vol. 6, p 275. (b) DePuy, C. H.; Damsauer, R.; Bowie, J. H.; Sheldon, J. C. *Acc. Chem. Res.* 1989, 20, 127. (c) Schwarz, H., ref 1, p 445.

(3) (a) Apeloig, Y.; Karni, M.; Stanger, A.; Schwarz, H.; Drewello, T.; Czekay, G. *J. Chem. Soc., Chem. Commun.* 1987, 989. (b) Hajdasz, D.; Squires, R. *J. Chem. Soc., Chem. Commun.* 1988, 1212. (c) Angelini, G.; Keheyon, Y.; Laguzzi, G.; Lilla, G. *Tetrahedron Lett.* 1988, 4159.

(4) Apeloig, Y.; Stanger, A. *J. Am. Chem. Soc.* 1987, 109, 272.

(5) Hoffmann, K. *J. Prakt. Chem.* 1981, 323, 399.

(6) Mayer, T. M.; Lampe, F. W. *J. Phys. Chem.* 1974, 78, 2433.

(7) Abernathy, R. N.; Lampe, F. W. *J. Am. Chem. Soc.* 1981, 103, 2573.

(8) Reuter, K. A.; Jacobson, D. B. *Organometallics* 1989, 8, 1126.

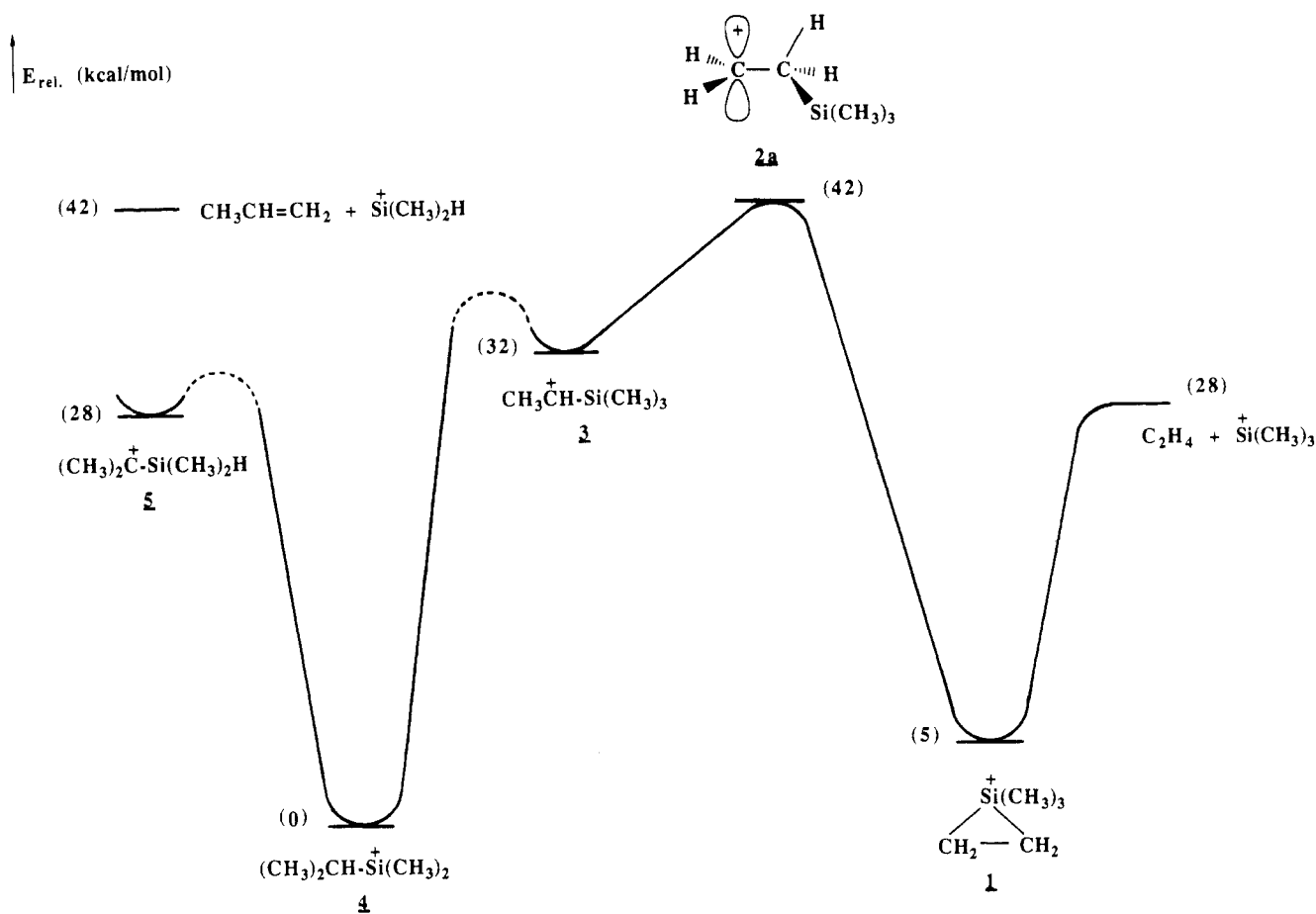(9) Levsen, K.; Schwarz, H. *Mass Spectrom. Rev.* 1983, 2, 77.

Scheme I. Schematic Potential Energy Diagram of Some $C_5H_{13}Si^+$ Isomers and Their Dissociation Products[a]

$E_{rel.}$ (kcal/mol)

2a

$$H_{I_{I_I}} \overset{(+)}{C} - C^{I_{I_I}} H \quad \text{with } H, H, \text{Si(CH}_3)_3$$

(42) —— $CH_3CH=CH_2 + \overset{+}{Si}(CH_3)_2H$

(42)

(32)

$CH_3\overset{+}{C}H\text{-Si(CH}_3)_3$

3

(28)

$(CH_3)_2\overset{+}{C}\text{-Si(CH}_3)_2H$

5

(28)

$C_2H_4 + \overset{+}{Si}(CH_3)_3$

(5)

$\overset{+}{Si}(CH_3)_3$

$CH_2 - CH_2$

1

(0)

$(CH_3)_2CH\text{-}\overset{+}{Si}(CH_3)_2$

4

[a] The relative energies are given in kcal/mol and are based on 6-31G*//3-21G calculations, corrected by substituent effects obtained from MP2/6-31G*//6-31G* calculations of the smaller $C_2H_7Si^+$ system.[3] **2a** is assumed to have an energy similar to that of the **3 → 2** transition structure. The latter could not be characterized directly due to the large size of the system.

base.[3b] In line with ab initio studies,[3a,10] this behavior is indicative of an ion structure with an intact but labile ethylene ligand. Both the bisected open (**2**) and silicon-bridged (**1**) structures are consistent with the observed

$\overset{+}{Si}(CH_3)_3$

$H^{I_I_I}C - C^{I_I_I}H$ with H, H, H

1

$Si(CH_3)_3$

$H_{I_I_I}\overset{(+)}{C} - C^{I_I_I}H$ with H, H, H

2

reactivity as well as with the previous finding[11] that dissociative ionization of D- and ^{13}C-labeled $(CH_3)_3SiCH_2CH_2OPh$ isotopomers (loss of PhO$^\bullet$) gives rise to labeled $C_5H_{13}Si^+$ ions in which the methylene groups in the ethylene unit are equilibrated.

While **1** and **2** are comparable in energy,[3,10a,b] both dissociation and isomerization of the two isomers are associated with significant barriers. In line with thermochemical data,[10d,12] **1** and/or **2** prefer to dissociate to the product combination $C_2H_4/Si(CH_3)_3^+$ rather than

$CH_3CH=CH_2/Si(CH_3)_2H^+$: According to ab initio MO theory[3a] the former is favored by 14.5 kcal/mol; this number can be compared with the rather wide range of experimental data of 14.4,[12a] 17.3,[12c] 20.0,[12b] and 23.6 kcal/mol.[10d] Isomerization of **1** to the substituted silicenium ion **4** (which lies 5 kcal/mol lower in energy), via **2a** and **3**, is also associated with an even larger barrier (see Scheme I); consequently, $(CH_3)_3SiCH_2CH_2^+$ (**2**) or its bridged form (**1**) do not interconvert with, for example, **4**. This is exactly borne out by the distinct bimolecular and the unimolecular reactions of **1** (**2**), reflecting the unique behavior of this $C_5H_{13}Si^+$ isomer.[3]

In contrast, the situation is more complex with the isomeric $C_5H_{13}Si^+$ species **3** and **4**. The ab initio finding,[3,13] that **3** is probably not a minimum on the potential energy surface of $C_5H_{13}Si^+$ (the observed shallow minimum at 3-21G is likely to be an artifact of this small basis set), is supported by various experimental observations:[3] Chloride abstraction from $CH_3CH(Cl)Si(CH_3)_3$ yields a mixture of ions **4** and **1** (**2**), resulting from competitive methyl and hydrogen shifts in the incipient $CH_3C^+(H)Si(CH_3)_3$ ion **3**.[3b] Furthermore, the CA mass spectra of $C_5H_{13}Si^+$ ions generated from either precursor $CH_3CH(Cl)Si(CH_3)_3$ or $(CH_3)_2CHSi(CH_3)_2Cl$ are virtually identical.[3a] Similarly, Angelini et al.[3c] found only trace amounts of $CH_3CH(O-CH_3)Si(CH_3)_3$ in the product mixture obtained in the gas-phase protonation of $(CH_3)_3SiCH=CH_2$ in the presence of methanol.

(10) (a) Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496. (b) Ibrahim, M. R.; Jorgensen, W. *Ibid.* **1989**, *111*, 819. (c) Apeloig, Y.; Arad, D. *Ibid.* **1985**, *107*, 5285. (d) For a recent experimental verification of the β-silicon effect, see: Li, Y.; Stone, J. A. *Ibid.* **1989**, *111*, 5586.

(11) Ciommer, B.; Schwarz, H. *J. Organomet. Chem.* **1983**, *244*, 319.

(12) (a) Krause, J. R.; Potzinger, P. *Int. J. Mass Spectrom. Ion Phys.* **1975**, *18*, 303. (b) Goodloe, G. W.; Austin, E. R.; Lampe, F. W. *J. Am. Chem. Soc.* **1979**, *101*, 3472. (c) Shin, S. K.; Beauchamp, J. L. *Ibid.* **1989**, *111*, 900.

(13) A. Stanger, Ph.D. Thesis, Technion, Haifa, 1985.

Table I. Isotopic Distribution for $C_2H_{4-x}D_x$ (x = 0–4) Generated in the Unimolecular Dissociation of Nascent $CH_3{}^+CHSi(CD_3)_3$

$C_2H_{4-x}D_x$ isotopomers, %	exptl results	calcd for complete H/D scrambling
C_2H_4	24.6	0.1
C_2H_3D	19.2	5.2
$C_2H_2D_2$	4.9	30.7
C_2HD_3	39.5	47.0
C_2D_4	11.8	17.0

An interesting prediction of the calculations is that the "nascent" ion **3** (e.g., generated by chloride abstraction from $CH_3CH(Cl)Si(CH_3)_3$) should collapse via methyl migration to the silicenium ion **4** while hydrogen migration leading to ion **1** (or **2**), which lies 27 kcal/mol lower in energy than **3**, faces a significant energy barrier of ca. 10 kcal/mol. This is unusual as exothermic or thermoneutral hydrogen shifts are usually facile processes. The barrier along the **3** → **1** (**2**) path results from the fact that a 1,2-hydrogen shift in **3** produces the eclipsed conformation **2a** (i.e., the dihedral angle HC^+CSi = $-30°$), which lies ca. 25–30 kcal/mol higher in energy than the perpendicular conformation **2** (i.e., HC^+CSi = $90°$).[10] In **2**, but not in **2a**, the empty $2p(C^+)$ orbital and the C–Si bond are properly aligned to interact (i.e., hyperconjugate),[10] to form the bridged form **1** and to fragment eventually to [$CH_2{=}CH_2$ + $(CH_3)_3Si^+$]. The cation **3** cannot fragment directly to produce $(CH_3)_3Si^+$, since the accompanying fragment, the carbene $CH_3CH:$, is very high in energy.

Results and Discussion

Here, we report further experimental evidence that strongly supports the implications of the ab initio calculations and in particular the existence of a significant energy barrier to the hydrogen shift connecting an α-silyl carbenium ion (e.g., **3**) and a β-silyl carbocation (e.g., **1** or **2**). From Scheme I it follows directly that the "nascent" ion **3** prior to unimolecular generation of $C_2H_4/Si(CH_3)_3{}^+$ should undergo significant methyl- and hydrogen-exchange processes involving the $Si(CH_3)_3{}^-$ and the CH_3CH part of **3**. This is precisely observed in the experiment.

Loss of HCl from gas-phase protonated $CH_3CH(Cl)Si(CH_3)_3$ generates a metastable $C_5H_{13}Si^+$ ion, which after mass selection in a ZAB-2F or ZAB-HF-3F mass spectrometer dissociates spontaneously (i.e., *without* collisional activation) exclusively to m/z 73 $(Si(CH_3)_3{}^+)$. A CIDI experiment[14] and the labeling results (to be described further below) leave no doubt that the neutral cogenerated in the reaction corresponds to C_2H_4, which, on energetic grounds, is ethylene and not vinylidene. The investigation of the mass-selected isotopomer $CH_3C^+(H)Si(CD_3)_3$ gives rise to the MIKE spectrum shown in Figure 1.

The isotopic distributions of $C_2H_{4-x}D_x$, extracted from Figure 1 and given in Table I, strongly suggest that part of the incipient $CH_3C^+(H)Si(CD_3)_3$ ions rearrange directly via the route **3** → **2a** → **1** (or **2**), thus giving rise to the formation of C_2H_4. Complete H/D exchange reactions occur to a small extent (16% based on a comparison of $C_2H_4/C_2H_2D_2$) only as evidenced by the weak signal for

$C_2H_{4-x}D_x$

Figure 1. MIKE spectrum of $CH_3C^+(H)Si(CD_3)_3$ (see text) generated from $CH_3CH(Cl)Si(CD_3)_3$ by chemical ionization (using CH_4 as reactant gas).

loss of $C_2H_2D_2$ (see Table I). However, the high proportion of C_2HD_3 generation (39.5%) requires the operation of a 1,2-methyl migration **3** → **4**, *prior* to the generation of **1** (**2**). To account for the formation of C_2D_4 (11.8%), methyl migration between the carbenium and silicenium centres must be reversible. In addition, the hydrogen-exchange processes within the CH_3CH/CH_2CH_2 parts of **3/2a/2** are also, to some extent (see below), reversible. This follows directly from the formations of C_2H_3D (19.2%), $C_2H_2D_2$ (4.9%), and C_2D_4 (11.8%).[16] However, as indicated by a comparison of the isotopic distributions observed experimentally with that calculated for a complete H/D scrambling (Table I), the latter is not achieved under the experimental conditions. This, very likely, reflects the fact that if **2a** is once reached, its probability to dissociate to $C_2H_4/(CH_3)_3Si^+$ (via vibrationally excited **1** or **2**) is much higher than for it to revert to **3** and **4**. Also, since the

(14) For CIDI (collisional-induced dissociative ionization) see: (a) Burgers, P. C.; Holmes, J. L.; Mommers, A. A.; Terlouw, J. K. *Chem. Phys. Lett.* **1983**, *102*, 1. (b) Wesdemiotis, C.; McLafferty, F. W. *Chem. Rev.* **1987**, *87*, 485. (c) Terlouw, J. K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 805. (d) Terlouw, J. K. *Adv. Mass Spectrom.* **1989**, *11*, 984. (e) Holmes, J. L. *Mass Spectrom. Rev.* **1989**, *6*, 513.

(15) For MIKE (mass-analyzed ion kinetic energy), see: Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, G. R. *Metastable Ions*; Elsevier: Amsterdam, 1973.
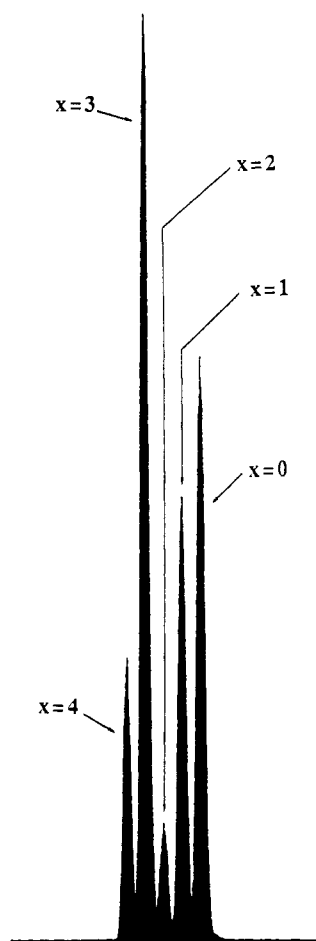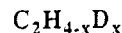
(16) The 4.9% of $C_2H_2D_2$ also requires the operation of extensive exchange processes. While it may be tempting to explain the genesis of the neutrals C_2H_3D, $C_2H_2D_2$, and C_2D_4 via the intermediacy of ion/dipole complexes[17] of the general type $[C_2H_4 \cdots {}^+Si(CH_3)_3] \rightleftharpoons [C_2H_4 \cdots {}^+H \cdots CH_2{=}Si(CH_3)_2] \rightleftharpoons [C_2H_5{}^+ \cdots CH_2{=}Si(CH_3)_2]$, comparison of the proton affinities of C_2H_4 (162 kcal/mol) versus $CH_2{=}Si(CH_3)_2$ (230 kcal/mol)[12c] makes this presumption an extremely unlikely one.

(17) There exist numerous precedents for ion/molecule complexes as intermediates in unimolecular reactions of cations in the gas phase. For selected references, see: (a) Morton, T. H. *Tetrahedron* **1982**, *38*, 3195. (b) McAdoo, D. J. *Mass Spectrom. Rev.* **1988**, *7*, 363, (c) Heinrich, N.; Schwarz, H. *Ion and Cluster Ion Spectroscopy and Structure*; Maier, J. P., Ed.; Elsevier: Amsterdam, 1989. (d) Hammerum, S. *J. Chem. Soc., Chem. Commun.* **1988**, 858.

Scheme II. Methyl Group and Hydrogen Atom Rearrangements Preceding the Dissociation of Silyl-Substituted Carbenium Ions
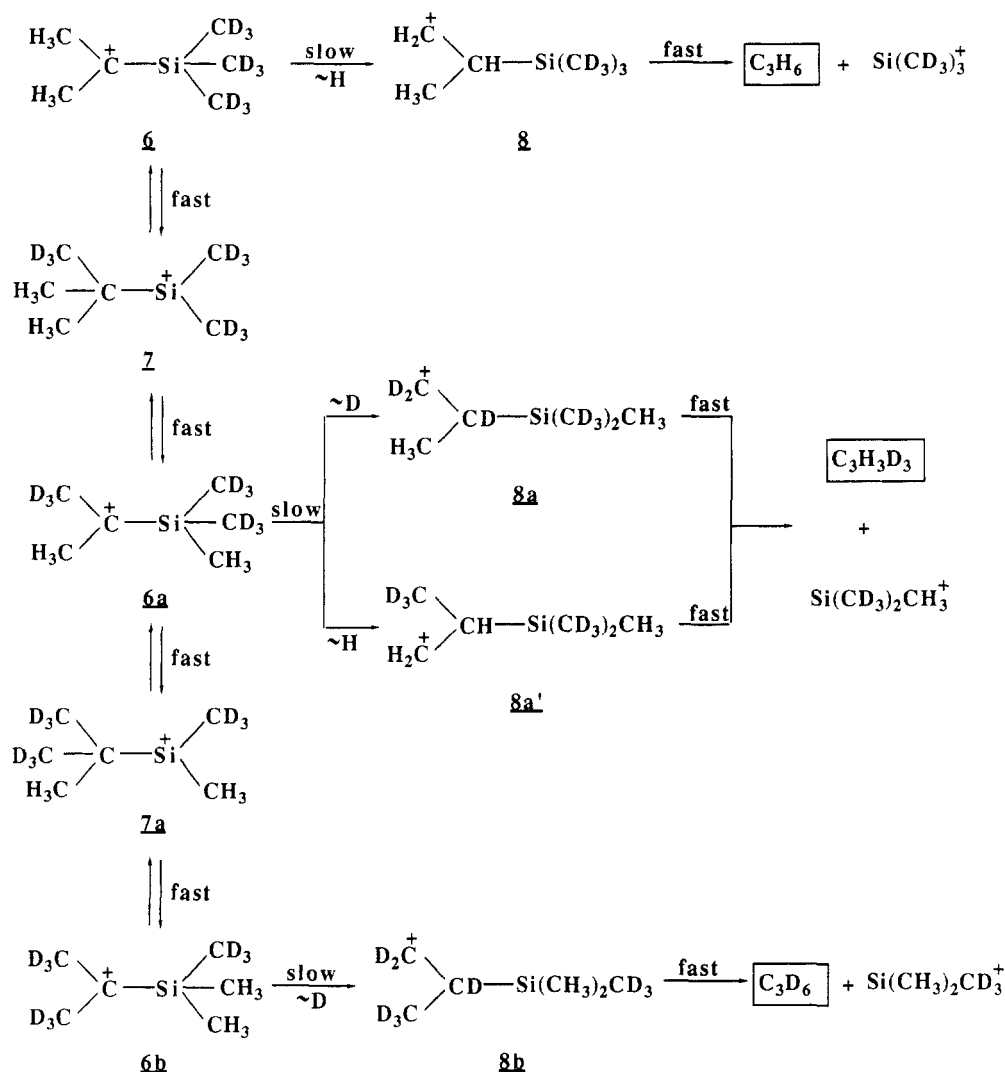
hydrogen shift **3** → **2a** is associated with the highest barrier, a kinetic isotope effect may be operative in this step. In fact we could reproduce the experimental intensity distribution by the following assumptions (see above): (1) Complete methyl scrambling occurs in **3**, i.e., **3** ⇌ **4** is a rapid process. (2) The (reversible) reaction **3** ⇌ **2a** occurs only *once* prior to dissociation, i.e., **3** → **2a** → **1** is much slower than **3** → **4**. (3) A kinetic isotope effect k_H/k_D of 2.5 operates in step **3** → **2a** → **1**. The calculated ratios for losses of $C_2H_4:C_2H_3D:C_2H_2D_2:C_2HD_3:C_2D_4$ are then 22:22:0:39:17; experimentally the ratios are 25:19:5:39:12. A second reversible reaction **3** ⇌ **2a** ⇌ **1**, occurring to a small extent followed by rapid methyl shifts, would explain the weak peak corresponding to loss of $C_2H_2D_2$. Also it would appear that the branching ratio for the methyl (**3** → **4**) vs the hydrogen migration (**3** → **2a**) is significantly greater than unity, and this agrees nicely with the results of Hajdasz and Squires,[3b] who from an analysis of ion/ molecule reaction products estimated a branching ratio of 4:1. If the fraction of complete H/D equilibration reactions can be taken as the inverse of the branching ratio, then we calculate for the branching ratio a value of ca. 5.

The present results do not permit us to draw conclusions as to whether **5** (which as **3** is probably not a minimum on the potential surface) is involved as a "dead end" in the formation of $C_2H_4/Si(CH_3)_3^+$. As already mentioned, under collision-free conditions we do not observe the product combination $CH_3CH=CH_2/(CH_3)_2SiH^+$, which,
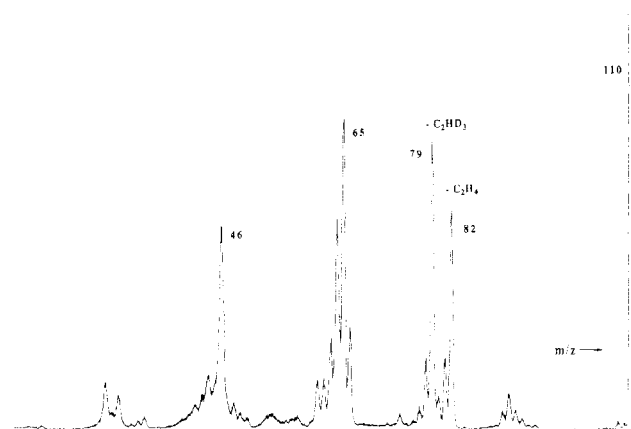
Figure 2. CA mass spectrum of $CH_3C^+(H)Si(CD_3)_3$ (see text).

however, is observed upon collisional activation.[3a]

Hence, our experimental results agree nicely with the ab initio calculations.[3a] What do these calculations predict for the stable ions, sampled by collisional activation? First, since the 1,2-hydrogen shift **3** → **2a** lies at an elevated energy level, is ought not to occur in stable ions. Second, ion **3** formed below the threshold for dissociation will rapidly rearrange to **4** because the activation energy for this reaction is small (if there exists a barrier at all). Ions **4** thus formed will not (or at best very slowly) rearrange
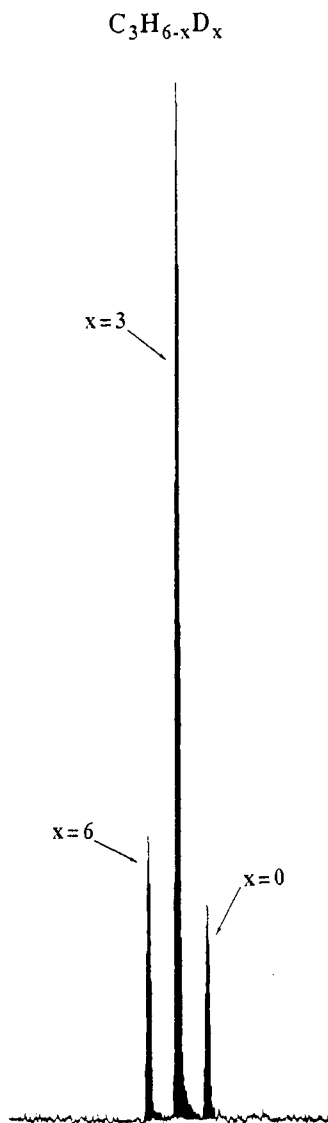
$$C_3H_{6-x}D_x$$

x = 3

x = 6

x = 0

Figure 3. MIKE spectrum of $(CH_3)_2C^+Si(CD_3)_3$ (see text) generated from $(CH_3)_2C(Cl)Si(CD_3)_3$ by chemical ionization (using i-C_4H_{10} as reactant gas).

back to **3** because the activation energy for this reaction is large (see Scheme I). Thus the calculations predict that " cold" nascent ion **3** will isomerize to **4**. This implies that there ought not to be significant methyl exchanges, and in fact the labeled ion CH_3-^+CH-$Si(CD_3)_3$ (**3d**) is expected to rearrange irreversibly to $(CH_3)(CD_3)CH$-$Si^+(CD_3)_2$. The CA mass spectrum of unlabeled **3** contains an intense peak at m/z 43 ($C_3H_7^+$ or $SiCH_3^+$) with no neighboring signals. For the labeled ion **3d** this signal is clearly shifted to m/z 46 (see Figure 2), and this shows that the rearranged ions are $(CH_3)(CD_3)CH$-$Si^+(CD_3)_2$ to the exclusion of $(CD_3)_2CH$-$Si^+(CH_3)(CD_3)$. That the reversible isomerization **3** $\rightleftarrows$ **2a** does not take place to a significant extent is indicated by the weak signals corresponding to losses of C_2H_3D and C_2D_4 vis-à-vis the intense signals for the

losses of C_2HD_3 and C_2H_4, whose intensity ratio incidentally approaches the 1:1 ratio expected on the basis of pure $(CH_3)(CD_3)CH$-$Si^+(CD_3)_2$. All these results are in good agreement with previous experimental observations[3] and theoretical calculations[3a,13] (Figure 2).

For metastable ions **3** the occurrence of very fast methyl shifts is, on first sight, obscured to some extent by the 1,2-hydrogen shifts, since combination of these processes leads to loss of all possible labeled ethylene molecules. It is clear then that if the tertiary H atom in **3** were to be replaced by CH_3, a much clearer picture ought to ensue. This is indeed what is observed experimentally.[18]

The MIKE spectrum of $(CH_3)_3C^+$-$Si(CH_3)_3$ contains only one signal which is due to the loss of C_3H_6, which on energetic grounds corresponds to propene. The MIKE spectrum of the labeled analogue, $(CH_3)_2C^+Si(CD_3)_3$, is given in Figure 3. This spectrum contains three signals that correspond to the losses of C_3H_6 (14%), $C_3H_3D_3$ (66%), and C_3D_6 (20%). For a complete scrambling of the five methyl groups according to Scheme II, one predicts a distribution of 10:60:30 for the losses of C_3H_6, $C_3H_3D_3$, and C_3D_6, respectively. Invoking an isotope effect of 2.5 in the transformation **6** $\rightarrow$ **8** leads to a calculated ratio of 15:66:19. Hydrogen-exchange processes between the methyl groups, which would be indicated by the formation of C_3H_{6-x} (x = 1, 2, 4, 5), are obviously too energy-demanding to compete efficiently with the fast methyl scrambling followed by dissociation. These results are in full harmony with the theoretical predictions that methyl migration to the silicenium ion $(CH_3)_3CSi^+(CH_3)_2$ is relatively facile while a hydrogen shift to produce the β-silyl-substituted carbenium ion $(CH_3)_3SiCH(CH_3)CH_2^+$ (which has a stability comparable to that of $(CH_3)_3CSi^+(CH_3)_2$) involves a significant energy barrier.[13] The origin of the barrier is stereoelectronic as discussed above for **2a**.

In conclusion, the present results provide further evidence for an efficient coupling of hydrogen/methyl migrations preceding unimolecular dissociations of silicon-containing cations in the gas phase. In fact for slowly dissociating ions methyl exchanges occur to the statistical limit.[19]

(18) Reported in part at the Second International Conference on Heteroatom Chemistry, Albany, NY, July 17–21, 1989.

(19) Complete methyl group scrambling, prior to losses of CH_4 and $(CH_3)_2SiO$ from $(CH_3)_3SiOSi(CH_3)_2^+$, was recently reported: Tobita, S.; Tajima, S.; Okada, F.; Mori, S.; Tabei, E.; Umemura, M. *Org. Mass Spectrom.*, in press.