

## Structure and Thermochemistry of $\beta$ -Silicon Carbenium Ions in the Gas Phase

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Both protonation of trimethylvinylsilane and addition of  $\text{Me}_3\text{Si}^+$  to ethylene in the gas phase produce the cation  $\text{Me}_3\text{Si}(\text{CH}_2\text{CH}_2)^+$ , with  $39 \text{ kcal mol}^{-1}$  stabilization energy relative to ethyl cation; however, chloride abstraction from  $\text{Me}_3\text{SiCHClCH}_3$  yields a mixture of ions resulting from competing methyl and hydrogen shifts in the nascent silylcarbenium ion.

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One of the most spectacular substituent effects in organic chemistry is the powerful stabilizing influence of a  $\beta$ -silyl group<sup>†</sup> on carbenium ion intermediates in solvolytic reactions. Numerous condensed-phase experimental investigations and computational studies of the so-called ' $\beta$ -silicon effect' have been carried out since the phenomenon was first noted by Ushakov and Itenberg in 1937.<sup>1-14</sup> We report here an

<sup>†</sup> The carbenium carbon atom is considered to be the  $\alpha$ -position.

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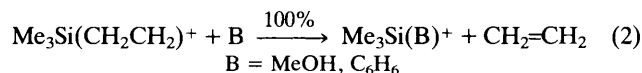
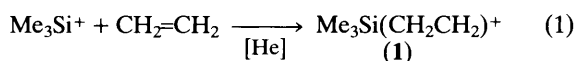
experimental determination of the extent of stabilization and structural consequences of both  $\alpha$ - and  $\beta$ -silyl substitution in simple gas-phase carbenium ions formed in a flowing after-glow-triple quadrupole apparatus at 298 K.<sup>‡</sup>

Our investigation concerns the family of ions  $\text{C}_5\text{H}_{13}\text{Si}^+$  ( $m/z$

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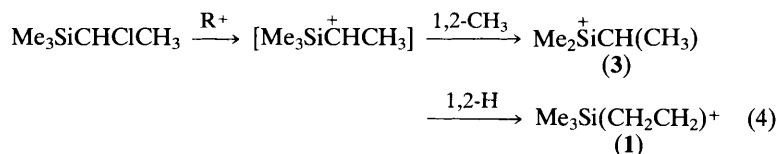
<sup>‡</sup> A complete description of the apparatus will be given in a future publication. For a preliminary account see ref. 15. All experiments were carried out using  $p(\text{He}) = 0.4 \text{ Torr}$ ;  $v(\text{He}) = 9400 \text{ cm s}^{-1}$ .

101) that can be generated in the helium flow reactor by several different methods. Reaction between trimethylsilylcenium ion (formed by electron ionization of  $\text{Me}_4\text{Si}$  or  $\text{Me}_6\text{Si}_2$ ) and ethylene at 0.4 Torr total pressure yields exclusively the termolecular addition product (1) [equation (1)]. This ion undergoes collision-induced dissociation (c.i.d.) in the triple quadrupole analyser by loss of ethylene with a measured energy threshold ( $E_T$ ) of  $0.8 \pm 0.1$  eV. § Collisional activation of the  $\text{C}_2\text{D}_4/\text{Me}_3\text{Si}^+$  adduct results in loss of only  $\text{C}_2\text{D}_4$ , showing that hydrogen scrambling does not take place within the ion. The bimolecular reactions of the ion (1) with methanol, benzene, and other  $n$ - or  $\pi$ -donor Lewis bases are relatively rapid ( $k = 2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ) and result mainly or exclusively in ethylene displacement<sup>17</sup> [equation (2)].

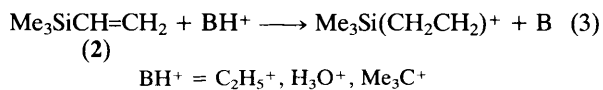


This behaviour is indicative of an ion structure with an intact but labile ethylene ligand. Both open (1a) and silicon-bridged (1b) structures are consistent with the observed reactivity. High-energy (3 kV) collisional activation experiments by Ciommer and Schwarz with  $^{13}\text{C}$ - and  $\text{CD}_2$ -labelled  $\text{C}_5\text{H}_{13}\text{Si}^+$  ions formed by dissociative ionization of  $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{OPh}$  derivatives show that the methylene groups in the ethylene ligand become equivalent prior to, or during c.i.d.<sup>12</sup> Moreover, *ab initio* calculations for both  $\text{H}_3\text{Si}(\text{CH}_2\text{CH}_2)^+$  and  $\text{Me}_3\text{Si}(\text{CH}_2\text{CH}_2)^+$  predict that the Si-bridged forms are lower in energy than the open forms.<sup>11,13</sup>

Protonation of trimethylvinylsilane  $\text{Me}_3\text{SiCH}=\text{CH}_2$  (2) by any of a variety of cationic Brønsted acids [equation (3)]



produces an ion  $\text{C}_5\text{H}_{13}\text{Si}^+$  that exhibits behaviour identical with that of the ion (1). Thus, protonated  $\text{Me}_3\text{SiCH}=\text{CH}_2$  undergoes c.i.d. by  $\text{C}_2\text{H}_4$  loss with a  $0.6 \pm 0.2$  eV energy threshold,<sup>§</sup> and reacts with MeOH,  $\text{C}_6\text{H}_6$ , and other Lewis bases by exclusive ethylene displacement.



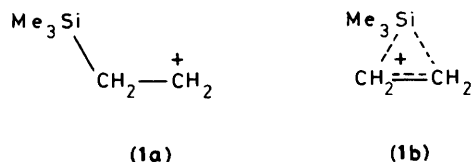
Exclusive  $\alpha$ -protonation of  $\text{Me}_3\text{SiCH}=\text{CH}_2$  yielding the ion (1) is required by the foregoing results since an 'authentic'  $\alpha$ -trimethylsilyl carbenium that would be derived from protonation  $\beta$  to silicon exhibits *different* unimolecular and bimolecular reactivity. For instance, the ion  $\text{C}_5\text{H}_{13}\text{Si}^+$  resulting from chloride abstraction from (or protonolysis of)  $\text{Me}_3\text{SiCHClCH}_3$  by  $\text{Me}_3\text{C}^+$  fragments in the triple quadrupole by loss of *both*  $\text{C}_2\text{H}_4$  and  $\text{C}_3\text{H}_6$  with similar yields, and reacts with

MeOH to yield an addition product *and* an ethylene displacement product in an approximately 4:1 yield ratio. Since neither  $\text{C}_3\text{H}_6$  loss nor adduct formation with MeOH are observed with protonated  $\text{Me}_3\text{SiCH}=\text{CH}_2$ , then formation of the  $\alpha$ -silyl carbenium ion by protonation  $\beta$  to silicon does not occur. This apparent selectivity is surprising in view of the fact that the developing carbenium ion formed by  $\alpha$ -protonation cannot fully benefit from the favourable bridging/hyperconjugative interactions of the  $\beta$ -silyl group since the vacant carbon 2p orbital and the C-Si bond are initially perpendicular.<sup>13</sup> A likely explanation is that the conjugate base of the protonating agent [B in equation (3)] mediates the proton transfer reaction in the ion/molecule collision complex by interacting with the nascent carbenium ion in a Lewis-base fashion.<sup>18</sup>

It can be shown that chloride loss from  $\text{Me}_3\text{SiCHClCH}_3$ , in fact, yields a *mixture* of isomeric ions arising from competing 1,2-H and 1,2-methyl shifts within the nascent  $\alpha$ -trimethylsilyl-carbenium ion [equation (4)]. An authentic ion  $\text{Me}_2\text{Si}^+\text{CH}(\text{CH}_3)_2$  (3) formed by chloride abstraction from the corresponding chlorosilane reacts with MeOH exclusively by addition, whereas the authentic hydrogen shift product (1) reacts exclusively by  $\text{C}_2\text{H}_4$  displacement. In a recent experimental and theoretical investigation of these same  $\text{C}_5\text{H}_{13}\text{Si}^+$  ions,<sup>13</sup> Apeloig, Schwarz, and their co-workers concluded that the trimethylsilyl carbenium ion rearranges entirely by the 1,2-methyl shift pathway to yield only (3), since the high energy collisional activation spectra of authentic (3) and the product of  $\text{Cl}^-$  loss from  $\text{Me}_3\text{SiCHClCH}_3$  were found to be identical. We also find the c.i.d. spectra of (3) and the ion mixture from  $\text{Me}_3\text{SiCHClCH}_3$  to be similar over a range of conditions of collision energy and target gas pressure in the triple quadrupole. Nevertheless, the results of the bimolecular reactions with MeOH clearly show that  $\text{Me}_3\text{SiCHClCH}_3$  produces a *mixture* of  $\text{C}_5\text{H}_{13}\text{Si}^+$  ions consisting of roughly 80% (3) and 20% (1).

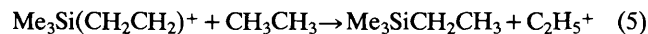
The total stabilization energy in the  $\beta$ -silyl carbenium ion (1) can be experimentally evaluated from the measured proton affinity (P.A.) of  $\text{Me}_3\text{SiCH}=\text{CH}_2$ . Proton transfer equilibrium involving  $\text{Me}_3\text{SiCH}=\text{CH}_2$  and  $\text{Me}_3\text{Si}(\text{CH}_2\text{CH}_2)^+$  cannot be established because of the strong tendency for  $\text{Me}_3\text{Si}(\text{CH}_2\text{CH}_2)^+$  to react by  $\text{C}_2\text{H}_4$  displacement rather than proton transfer with most reference bases. However, by combining a conventional proton affinity bracketing approach<sup>19</sup> with careful monitoring of the kinetic energy dependence of proton transfer reactions taking place in the triple quadrupole collision chamber,<sup>20</sup> we have arrived at a consistent value for P.A. ( $\text{Me}_3\text{SiCH}=\text{CH}_2$ ) of  $199 \pm 2$  kcal mol<sup>-1</sup>.

A proton affinity of 199 kcal mol<sup>-1</sup> ranks  $\text{Me}_3\text{SiCH}=\text{CH}_2$  among isobutene (P.A. 196), tetramethylethylene (P.A. 199) and styrene (P.A. 202 kcal mol<sup>-1</sup>) with respect to base



§ Energy thresholds for fragmentation reactions are determined under single collision conditions in the middle quadrupole from a linear fit of the steeply rising portion of a plot of normalized product ion intensity *versus* centre-of-mass collision energy. The energy axis origin is located with retarding potential analysis and the apparent thresholds are corrected for Doppler broadening.<sup>16</sup>

strength.<sup>19</sup> Therefore the total stabilization energy of the ion (1) relative to protonated ethylene (P.A. 162.6 kcal mol<sup>-1</sup>)<sup>19</sup> is similar to that of tertiary and benzylic carbenium ions. The stabilization energy relative to hydrogen in an ethyl cation is formally given by the hypothetical hydride transfer reaction in equation (5).<sup>10</sup> Using  $\Delta H_f(1) = 138 \pm 4$  kcal mol<sup>-1</sup> derived from the measured proton affinity and an estimate for  $\Delta H_f(\text{Me}_3\text{SiEt})$ ,<sup>¶</sup> we compute  $\Delta H(5) = 39$  kcal mol<sup>-1</sup>. This is in good agreement with the theoretical stabilization energy for  $\text{H}_3\text{Si}(\text{CH}_2\text{CH}_2)^+$  of 38 kcal mol<sup>-1</sup> reported by Jørgensen and co-workers.<sup>11</sup>



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¶  $\Delta H_f(\text{Me}_3\text{SiCH}=\text{CH}_2, \text{g}) = -29 \pm 3$  kcal mol<sup>-1</sup>;  $\Delta H_f(\text{Me}_3\text{SiCH}_2\text{CH}_3, \text{g}) = -59 \pm 2$  kcal mol<sup>-1</sup> estimates based on  $\Delta H_f(\text{Me}_4\text{Si}, \text{g}) = -54.1 \pm 1.1$  kcal mol<sup>-1</sup><sup>21</sup> and assumed energy increments for replacing methyl with ethyl and vinyl; cf. ref. 22.