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The trimethylsilylation of acetylene

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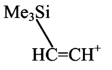
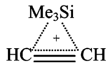
The gas-phase reaction of Me_3Si^+ ions with acetylene is remarkably sensitive to the environment, leading to substitution products in radiolytic systems at atmospheric pressure and to rearranged adduct ions in the FT-ICR cell at 10^{-8} Torr, while seeming unproductive in an intermediate pressure range.

The ion molecule reactions of Me_3Si^+ ions, easily accessible species in the gas phase, provide an entry into the rich chemistry of organosilicon cations, a subject of significant current interest.[1] This interest is based in part on the fact that a silyl substituent may exert conspicuous effects on the stability of carbocations as shown by several α- and β-silyl-substituted carbocations. For example, incipient α-silyl-substituted carbenium ions, $Me_3SiCHCH_3^+$, generated in the gas phase from different precursors, give a mixture of isomeric ions by 1,2-H and 1,2-Me migrations, as clarified by mass spectrometric and computational studies.[2–4] Conversely, stable silyl-substituted vinyl cations have been observed in the gas phase, where α-silylvinyl cations, $Me_3SiC{=}CH_2^+$, could be produced by MS and identified as distinct species.[5]

Recently, silyl-substituted unsaturated carbocations have been even invoked as intermediates in the formation of neutral silylated products arising from the reaction of radiolytically formed Me_3Si^+ with alkynes in a gaseous medium at atmospheric pressure.[6] In the exemplary reaction of Me_3Si^+ with acetylene the deprotonation of Me_3Si^+–acetylene adduct, described either as the open species (**A**) or as the bridged structure (**B**), produced high yields of $Me_3SiC{\equiv}CH$.


(A)


(B)

This result stands in contrast with the report of a high-pressure mass spectrometric (HPMS) study of the same reaction which failed to produce any detectable abundance of the Me_3Si^+–acetylene adduct.[7] The reason for this failure was ascribed to the unfavourable thermodynamics for the binding of Me_3Si^+ with acetylene relative to water. Traces of adventitious water made this ligand a too effective competitor. However, in the same high-pressure ion source the equilibria for the association of Me_3Si^+ with alkenes[8] and higher alkynes[7] were fully characterized. In particular, the thermodynamic parameters for the association with ethylene were determined, namely a $\Delta H°$ value of -23.6 kcal mol^{-1} and a $\Delta S°$ value of -38.5 cal K^{-1} mol^{-1}. These data are consistent with the high yield of $Me_3SiCH{=}CH_2$ formed by the radiolytic reaction of Me_3Si^+ with C_2H_4 at the partial pressure of 5 Torr.[6] At the same time they predict the equilibrium to lie on the reactant side at *ca.* 5×10^{-8} Torr C_2H_4, the operative pressure in Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. Accordingly Me_3Si^+ appears unreactive with C_2H_4 by FT-ICR. Along this line of reasoning it was quite unexpected to find that Me_3Si^+ does indeed react with C_2H_2 and higher homologues in FT-ICR, yielding a formal adduct ion.[9] Collision induced dissociation (CID) and ion–molecule reactions have been used to probe the structure of the $C_5H_{11}Si^+$ ions at m/z 99 that are formed by the Me_3Si^+ reaction with C_2H_2 in the FT-ICR cell at 4×10^{-8} Torr [eqn. (1)]. The bimolecular rate constant k equal to $1.3\ (\pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} shows that the reaction is relatively inefficient (eff = k/k_{coll} = 0.013), leading exclusively to $C_5H_{11}Si^+$ ions (**1**).

$$Me_3Si^+ + HC{\equiv}CH \rightarrow C_5H_{11}Si^+ \qquad (1)$$

‘On resonance’ CID of **1** shows the fragmentations to $SiC_2H_7^+$ + C_3H_4 (60%) and to $SiC_3H_9^+$ + C_2H_2 (40%) as dominant channels. Even if CID results do not offer a conclusive evidence of ion structure, the detection of $SiC_2H_7^+$ indicates the formation of a covalent Si–C bond within **1**.

The presence of an intact acetylene ligand can be excluded on the basis of the bimolecular reactivity of **1** towards stronger Lewis bases, such as propyne and acetone. In fact these compounds are found unable to displace acetylene to give the corresponding trimethylsilylated adduct.

Also water is unable to give a silylated adduct, rather, it reacts relatively rapidly (k = $2.2\ (\pm 0.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) and specifically by the exclusive elimination of C_3H_6 and concomitant formation of Me_2SiOH^+ at m/z 75 [eqn. (2)].

$$\mathbf{1} + H_2O \rightarrow Me_2SiOH^+ + C_3H_6 \qquad (2)$$

It may be mentioned that when the Me_3Si^+–acetone adduct, containing an intact trimethylsilyl group, is allowed to react with water no detectable formation of any m/z 75 product was observed.

All these findings point to a nascent Me_3Si^+–acetylene species that has entirely rearranged into a more stable silylenium ion, $[Me_2SiC_3H_5]^+$, by methyl transfer from Si to C with ensuing charge localization on silicon. In the H_3Si^+–acetylene model reaction, *ab initio* calculations have shown that the H_3Si^+–acetylene adduct may undergo a two-step isomerization to the more stable 1-silaallyl cation.[10] This rearrangement requires passing beyond a significant barrier. The top of the barrier, however, lies below the energy level of the H_3Si^+–acetylene couple. On the assumption that a similar potential energy diagram holds also for the Me_3Si^+–acetylene system under study, the same isomerization process to 1-silaallyl cation should take place. In fact, the interaction energy released in the formation of the Me_3Si^+–acetylene adduct, and stored as internal energy of the complex, allows the primary adduct (A or B) to overcome the barrier for the isomerization to a Si-centered cation. This is obviously due to the absence of efficient collisional deactivation at the low pressure of the FT-ICR cell.

To gain further insight into the isomerization process leading to **1**, model ions were sought by protonation or dissociative ionization of suitable precursors.

The protonation of trimethylsilylacetylene, $Me_3Si{-}C{\equiv}CH$, by any of a variety of cationic Brønsted acids, AH^+, produces a mixture of ions whose relative abundances depend on the gas phase basicity of A. An ion corresponding to the protonated species at m/z 99, $C_5H_{11}Si^+$ is detected, in noticeable amounts when A is C_3H_6 or i-C_4H_8. This ion exhibits CID mass spectra and bimolecular behavior with water and propyne identical to that of **1**. These FT-ICR results testify that the silyl-substituted

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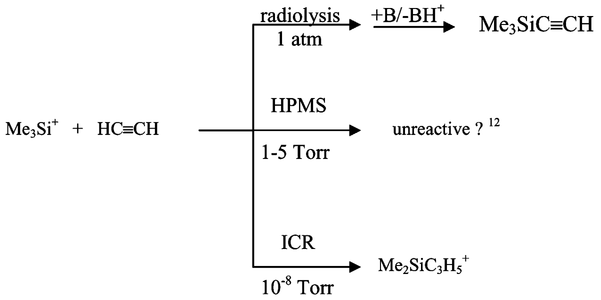
vinyl cation $Me_3SiC_2H_2^+$, which is generated by protonation, may store enough internal energy to dissociate to reagents and/or to undergo isomerization.

Isomeric ions such as $Me_2SiC(CH_3){=}CH_2^+$ (**2**) and $Me_2SiCH{=}CH(CH_3)^+$ (**3**), formed by 25 eV electron bombardment of $Me_3SiC(CH_3){=}CH_2$ and *trans*-$Me_3SiCH{=}CH(CH_3)$, respectively, have also been investigated. The reaction of each species with water gave product ions at *m*/*z* 75 by loss of C_3H_6 at the same rate shown by **1**, namely $k = 2.0\ (\pm 0.5) \times 10^{-10}$ cm^3 molecule s^{-1}.

Whereas the formation of **2** from the Me_3Si^+–acetylene adduct should involve a 1,2-hydrogen migration preceding a 1,2-methyl transfer, the formation of **3** might result from **2** by a reversible β-hydrogen migration/alkyne insertion process, in analogy to the reaction pathway connecting $Me_2Si(i\text{-}C_3H_7)^+$ and $Me_2Si(n\text{-}C_3H_7)^+$.[4] A further possible route, the rearrangement of Me_3Si^+–acetylene to $Me_2SiCH{=}CH(CH_3)^+$ by 1,3-methyl transfer is highly unlikely because it should involve a high kinetic barrier.[2]

In conclusion, the reaction of Me_3Si^+ with acetylene provides a neat example of the role of the environment, notably the operative pressures, on the course of ion–molecule reactions in the gas phase. In the radiolytic approach, the presence of a neutral (M) at 5–50 Torr favors the formation of adduct ions, such as Me_3Si^+–M, that rapidly reach thermal equilibration with the environment due to frequent unreactive collisions with a bulk gas at the typical pressure of 1 atm. Any excess energy released in the formation of the adduct from the separated reactants may thus be dissipated before any rearrangement or fragmentation process is allowed to occur. This behavior is shown in the reaction of Me_3Si^+ with both C_2H_2 and C_2H_4 leading to adduct ions that survive long enough to be deprotonated by an added base and yield the corresponding substitution products.[6] At the other extreme, the 10^{-8} Torr pressure of M, that is typical of FT-ICR conditions, prevents any efficient collisional cooling, and adduct ions retain the energy to undergo back dissociation. The Me_3Si^+ reaction with acetylene succeeds in leading to long-lived adducts shown to have the structure of rearranged Me_2Si–$C_3H_5^+$ ions. The access to these more stable isomers is permitted by an energy barrier that lies below the energy level of the reactant pair. Conversely, the barrier for the isomerization of Me_3Si^+–ethylene is computed to rise above the energy of the $Me_3Si^+ + C_2H_4$ couple[2] and therefore Me_3Si^+ behaves as unreactive with ethylene in FT-ICR. At the intermediate pressures of HPMS or of flowing afterglow techniques, adduct ions such as Me_3Si^+–ethylene may be collisionally stabilized[8,11] but, within this range, in certain cases the relative pressures may be such as to obscure the formation of possible significant products.[8]



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9 In the FT-ICR experiments, performed on a Bruker Spectrospin Apex TM 47e mass spectrometer equipped with a 4.7 T superconducting magnet, Me_3Si^+ cations were generated by ionization of CH_4–$SiMe_4$ (99.5 : 0.5) mixtures in the external chemical ionization source at $\sim 4 \times 10^{-5}$ Torr (1 Torr = 133 Pa) and transferred into the 'infinity' cell containing a known pressure, typically in the range of 1–5×10^{-8} Torr, of the neutral reagent.

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