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# Isomeric $C_5H_{11}Si^+$ ions from the trimethylsilylation of acetylene: An experimental and theoretical study

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Dedicated to the memory of Detlef Schröder.

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#### ABSTRACT

The gas phase offers a unique medium to conduct the electrophilic addition reaction of  $(CH_3)_3 Si^+$ (trimethylsilylium ion) to acetylene. However, this deceptively simple reaction displays a remarkable dependence on the gas phase pressure, revealing the interplay of competitive pathways. In FT-ICR mass spectrometry at ca  $10^{-8}$  mbar, the nascent  $(CH_3)_3$ Si<sup>+</sup>-acetylene complex undergoes a rearrangement process yielding the  $CH_2=C(CH_3)-Si(CH_3)_2^+$  ion. This structure has been assigned on the basis of the ion-molecule reactivity displayed by the sampled  $C_5H_{11}Si^+$  adducts, matching the one of the model ion obtained from 2-(trimethylsilyl)propene. Whereas the absolute values of kinetic rate constants could not discriminate between isomeric species, the branching ratios for competitive addition-elimination channels in the reaction with *i*-C<sub>3</sub>H<sub>7</sub>OH and *t*-C<sub>4</sub>H<sub>9</sub>OCH<sub>3</sub> were found to be diagnostic of different structures. The pathways leading from the (CH<sub>3</sub>)<sub>3</sub>Si<sup>+</sup>-acetylene complex primarily formed to the candidate  $C_5H_{11}Si^+$  isomers have been investigated by ab initio quantum chemical calculations at CCSD(T)/6-311 ++G(2d,2p)//B3LYP/6-311G(2d,p) level. The energy profiles show that the path to the  $CH_2=C(CH_3)-Si(CH_3)_2^+$  isomer is associated to the lowest activation energy barrier, below the reactants energy level. The energy released in the (CH<sub>3</sub>)<sub>3</sub>Si<sup>+</sup>-acetylene association process, remaining stored in the complex formed at low pressure, thus allows the isomerization to a species holding the positive charge on electropositive silicon. Interestingly, the most stable of the conceivable isomers, (E)- $(CH_3)$ —CH=CH=Si(CH\_3)<sub>2</sub><sup>+</sup>, is not accessed because of an activation energy barrier protruding above the reactants energy level. The combined information of ion-molecule reactivity and ab initio calculations of potential isomers and rearrangement pathways has thus afforded a comprehensive view of the (CH<sub>3</sub>)<sub>3</sub>Si<sup>+</sup> addition reaction to acetylene under various pressure regimes.

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#### 1. Introduction

The electrophilic silylation of hydrocarbons can in principle be obtained by delivering a formal  $R_3Si^+$  species on an unsaturated compound. However, the neat process is not easily accomplished in solution. Indeed, trivalent  $R_3Si^+$  silylium ions are hardly accessible in condensed phases due to their high reactivity and enormous electrophilicity, though being thermodynamically more stable than equally substituted carbenium ions [1–12]. In recent years considerable efforts have been devoted to the development of powerful sources of " $R_3Si^+$ " and conventional trialkylsilyl triflate reagents have been surpassed by reagents based on carborane anions [13]. Although the R<sub>3</sub>Si (carborane) species do not contain free silvlium ions they may react like silylium ions. Still, the silylation of a weak base such as benzene has yet to be established in the condensed phase [13–15]. An ideal environment where R<sub>3</sub>Si<sup>+</sup> ions can be easily generated and studied is the gas phase [16,17] In this medium the formation of trimethylsilylbenzene from the reaction of (CH<sub>3</sub>)<sub>3</sub>Si<sup>+</sup> with benzene and neutralization by a strong nitrogen base was obtained [18-22]. In this gas phase work it was recognized for the first time that the formation of the intermediate silylated  $\sigma$ complex was promptly achieved but the critical step to obtain neutral phenylsilane was the deprotonation of the intermediate. Following these gas phase studies demonstrating the key role of deprotonation, the aromatic silvlation of toluene by R<sub>3</sub>SiCl under AlCl<sub>3</sub> catalysis has been successfully accomplished in the presence of hindered tertiary amines by Olah et al, although in only moderate yield [23]. In the gas phase, not only benzene but also toluene and

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other aromatic and heteroaromatic compounds have been successfully silylated [24–28]. The silylium ions were formed in a gaseous environment at atmospheric pressure using a radiolytic approach [29]. Also a nucleogenic approach based on the  $\beta$ -decay of tritium has been used to generate silylium ions in the gas phase and the reaction with  $\pi$ -nucleophiles has been reported [30–33]. pressure, the adduct ions,  $[(CH_3)_3Si^+$ -acetylene complex]\*, primarily excited by the exothermicity of the formation process (step (*a*) in Eq. (2)), undergo an efficient cooling by collisions with unreactive molecules (M) of the bath gas (step (*b*) in Eq. (2)), thus allowing the formation of thermalyzed adduct ions,  $[(CH_3)_3Si^+$ -acetylene complex], that can subsequently be deprotonated to yield the substitution product (CH<sub>3</sub>)\_3SiC=CH (step (*c*) in Eq. (2)) [34].

$$(CH_{3})_{3}Si^{+} + HC \equiv CH \xrightarrow{(a)} [(CH_{3})_{3}Si^{+} - acetylene \ complex]^{*} \xrightarrow{(b)} [(CH_{3})_{3}Si^{+} - acetilene \ complex] \xrightarrow{(c)} +B \\ -H^{+} \\ (CH_{3})_{3}Si^{-} - acetilene \ complex] \xrightarrow{(c)} +B \\ -BH^{+} \\ (CH_{3})_{3}SiC \equiv CH \\ (CH_{3})_{$$

In the gas phase at atmospheric pressure  $(CH_3)_3Si^+$  ions are found to react with acetylene yielding a substitution product, namely  $(CH_3)_3SiC=CH$  [34]. However, mass spectrometric studies on the reaction of  $(CH_3)_3Si^+$  with acetylene have yielded apparently contrasting results. In high pressure mass spectrometry (HPMS) operating at 3–5 mbar, Me<sub>3</sub>Si<sup>+</sup> appears to be unreactive with acetylene (i.e. it does not yield the expected adduct ion) and the ion is ultimately captured by adventitious water [35], a potent nucleophile toward silylium ions. Quite in contrast, operating at  $10^{-8}-10^{-7}$  mbar in the cell of an FT-ICR mass spectrometer, the formation of an adduct ion at m/z 99 from the reaction of  $(CH_3)_3Si^+$ with acetylene has been reported to occur [36], albeit with low efficiency (0.013, as measured by the ratio  $k_{exp}/k_{coll}$ , where  $k_{exp}$  is the bimolecular rate constant for reaction (1) and  $k_{coll}$  is the calculated collision rate constant) [37].

$$(CH_3)_3 Si^+ + HC \equiv CH \rightarrow C_5 H_{11} Si^+$$

$$m/z \, ^{99}$$
(1)

The nascent ionic addition product from the reaction of  $(CH_3)_3Si^+$  with acetylene may be assigned the structure of an unrearranged species with the features of a  $\beta$ -silyl-substituted vinyl cation (**1A**), possibly acquiring a cyclic geometry (**1B**) [38–41].

 $\beta$ -silyl hyperconjugative stabilization of vinly cations is well documented. In solution  $\beta$ -silyl-substituted vinyl cation can be generated by protonation of silyl substituted allenes [42] and silyl substituted alkynes [43–46] under carefully controlled experimental conditions in non-nucleophilic solvents and by addition of inicipient silylium ions to alkynes in the presence of inert counterions [47–49]. The determination of the X-ray structure of a vinyl cation stabilized by two  $\beta$ -silyl substituents has also been achieved [50].

The  $\beta$ -silvl effect, stabilizing a positively charged carbon, exerts a strong influence on gaseous carbenium ions [51-57] and the formation of an intermediate resembling 1A or 1B is inferred from the formation of the  $(CH_3)_3SiC \equiv CH$  substitution product in the experiments at atmospheric pressure, run in the presence of a strong base [34]. However, the structure of the adduct at m/z 99 formed in the FT-ICR cell does not respond to any kind of behavior expected from a species like 1A or 1B. For example, the reaction with water, expected to yield (CH<sub>3</sub>)<sub>3</sub>SiOH<sub>2</sub><sup>+</sup> by (CH<sub>3</sub>)<sub>3</sub>Si<sup>+</sup> transfer to the oxygen nucleophile, leads rather to (CH<sub>3</sub>)<sub>2</sub>SiOH<sup>+</sup> with concomitant loss of C<sub>3</sub>H<sub>6</sub>, an indication that a rearrangement process has taken place. The same C<sub>3</sub>H<sub>6</sub> neutral is lost in collision induced dissociation (CID) as the prevailing fragmentation channel. A unifying justification for the observed reactivity pattern has been put forward, based on the different pressure range prevailing in the three experiments, as illustrated in Eq. (2) [36]. At nearly atmospheric In the 3-5 mbar environment of the HPMS experiments the [(CH<sub>3</sub>)<sub>3</sub>Si<sup>+</sup>-acetylene complex] is apparently a fleeting species, undergoing fast desilylation by ubiquitous water. However, it is only at the  $10^{-8}$ – $10^{-7}$  mbar pressure in the FT-ICR cell that the excess energy released in the adduct ion may not be dissipated (unless by radiative emission, a poorly efficient process in a small molecule) [58-60] and remains available to surmount the activation energy barriers leading to rearranged ions C5H11Si<sup>+</sup> (step (e) in Eq. (2)). The latter species, that reasonably lie in a deeper energy well, become resistant to dissociation under the prevailing environmental conditions. Probing these suggested rearrangement processes and uncovering the structure of the end product ions was the aim of the present contribution. The problem has been tackled with a combined approach based on bimolecular ion-molecule reactions with appropriate neutrals as diagnostic tools to test ion structures and on ab initio calculations to assist in assigning plausible rearrangement pathways. The study of this system (namely  $(CH_3)_3Si^+ + HC \equiv CH)$  lends itself to uncover important issues in the reactivity of silyl-substituted carbenium ions and silacations such as the thermodynamic drive to the most stable species on the  $C_5H_{11}Si^+$  potential energy surface, the electronic factors affecting their stability, the kinetic barriers involved in the rearrangement processes, representing a number of fundamental questions about the chemistry of these reactive intermediates.

#### 2. Experimental details

#### 2.1. Materials

The hydrocarbons CH<sub>4</sub>,  $C_2H_2$ , and  $C_3H_8$  were high-purity (99.9 mol%) gases from Matheson Gas Products Inc. The other chemicals used as reagents or as precursors of desired ions were purchased from Sigma–Aldrich. The silylated alkenes that were not commercially available were prepared from the Wurtz–Fittig reaction of (CH<sub>3</sub>)<sub>3</sub>SiCl with the appropriate alkenyl bromide [61] and were purified by preparative GLC using a 4-m long, 4-mm i.d. stainless steel column, packed with 5% DC 200 methylsilicone on Supelcoport. Their identity was verified by NMR spectroscopy and mass spectrometry.

#### 2.2. FT-ICR mass spectrometry

The experiments were performed with a Bruker Spectrospin Apex TM 47e mass spectrometer equipped with a cylindrical "infinity" cell within a 4.7 T superconducting magnet and with an external ion source. In this source, the chemical ionization (CI) of a neutral admitted through a probe for volatile compounds is effected by the ions of a chosen CI reagent, ionized by a 200 eV electron beam. The ions formed in the external source are led into the FT-ICR cell by an ion guide that should not impart any excess translational energy to the ions. The ions can be further allowed to equilibrate at the room temperature of the FT-ICR cell by unreactive collisions with argon, admitted in the cell at  $10^{-5}$  mbar by a pulsed valve. After a delay time the ions of interest were selected by ejecting unwanted ions using rf sweeps and single shots. The selected ions were then let to react with a neutral reagent leaked in the cell by a needle valve at a constant pressure, typically in the range of  $10^{-8}$ – $10^{-7}$  mbar. The pressure readings were obtained by a cold cathode gauge calibrated using the rate constant value of  $1.1 \times 10^{-9}$  cm<sup>3</sup> s<sup>-1</sup> for the reference reaction  $CH_4^{\bullet^+} + CH_4 \rightarrow CH_3^{\bullet} + CH_5^+$ , and corrected using individual response factors [62,63]. The kinetics of the ionmolecule reactions were monitored by recording 10-20 averaged scans for each mass spectrum in series of runs corresponding to increasing reaction time. In these conditions the kinetics are pseudo first order and the rate constants  $(k_{obs})$  were obtained from the slope of the semilogarithmic decrease of reactant ion abundance versus reaction time. The pseudo first order rate constants divided by the substrate concentration yield the bimolecular rate constants  $(k_{exp})$ . Their values are having an estimated error ( $\pm$ 30%) largely due to the uncertainty affecting the pressure reading of the neutral. The reported  $k_{exp}$  values are the average of at least three values for kinetic runs at different neutral pressure. The reaction efficiencies ( $\Phi$ ) were calculated as % ratio of  $k_{exp}$  relative to the collision rate constant  $(k_c)$  calculated by the parameterized trajectory theory [37]. The elemental composition of the product ions was verified by m/z measurements at high resolution.

#### 2.3. Computational details

The quantum chemical calculations were performed using the Gaussian 09 suites of programs [64]. All structures were fully optimized using standard methods (density functional theory (DFT) hybrid methods with the B3LYP functional). The 6-311G(2d,p) basis set was used for geometry optimizations and frequency calculations. Analytical vibrational analyses at the same level were performed to determine the zero-point vibrational energy (ZPE) and to ascertain each stationary point as a minimum or first-order saddle point. Corrections for ZPE (not scaled) are included in the calculated energies. All transition states were found by using QST2 and QST3 methods and their correct connection with the relative reagents and products was verified by means of intrinsic reaction coordinate calculations [65,66]. Extra valence functions and polarization functions as in the 6-311++G(2d,2p) basis set were used to allow CCSD(T)/6-311++G(2d,2p) energy calculations of B3LYP/6-311G(2d,p) optimized geometries.

In order to further check the reliability of the obtained geometries, MP2 optimizations have also been performed with the same basis set on few exemplary structures. MP2/6-311G(2d,p) geometries display very small differences, showing that B3LYP/6-311G(2d,p) can give a good description of the geometrical features of the investigated system. Thus, the relative energies, interconversion pathways and transition state structures that are finally reported were evaluated at CCSD(T)/6-311++G(2d,2p)//B3LYP/6-311G(2d,p) level of theory.

#### 3. Results and discussion

#### 3.1. Sample ion(s) and model ions

The ion (or, possibly, ion mixture) of interest is the adduct at m/z 99 formed from the addition of  $(CH_3)_3Si^+$  (obtained by chemical ionization of  $(CH_3)_4Si$  using  $CH_4$  gas) to acetylene in the cell of an FT-ICR mass spectrometer, henceforth named sample ion(s) **S**. In order to obtain experimental information that could allow a structural assignment to this species, model ions



were sought whose reactivity behavior, compared with that of the sample ion S, can yield diagnostic information. To this end a number of Me<sub>3</sub>Si-substituted propenes have been synthesized, namely 2-(trimethylsilyl)propene, allyltrimethylsilane, (E)- and (Z)-1-(trimethylsilyl)propene. The chemical ionization (CI) using C<sub>3</sub>H<sub>8</sub> as neutral precursor of reagent C<sub>3</sub>H<sub>7</sub><sup>+</sup> ions forms abundant C<sub>5</sub>H<sub>11</sub>Si<sup>+</sup> product ions that are expected to retain the structure of the parent neutrals. The ensuing species (labeled 2,3,4,6) are depicted in Chart 1 together with the trimethylsilyl cation complex with acetylene (1) and a  $\alpha$ -silvlvinyl cation (5) that may be involved as transient intermediate. Their reactivity behavior toward selected reagents is demonstrated to be quite distinct for each one of them (with the possible exception of the (E)- and (Z)isomers of 1-propenyl-dimethylsilyl cation, i. e. 2 and 4), supporting the idea that the mild CI by  $C_3H_7^+$  ions, while able to abstract a methide anion [16,67], does not confer any excess energy to the incipient silyl cation that could activate subsequent rearrangement processes. The notable stability of the silicon containing cations, in which the charge is located on a silicon atom, is the driving force of the reaction, as found responsible for example for the facile cleavage of a Si-C bond in radical cations [17,68]. The distinct behavior of so-formed species **2,3,4,6** (and therefore their distinct structure) is retained also when they are formed by the more fierce CI by CH<sub>5</sub><sup>+</sup> ions and, conversely, when the ions are submitted to collisional relaxation by a pulse of argon at  $10^{-5}$  bar.

#### 3.2. Ion-molecule reactions of $C_5H_{11}Si^+$ ions

CID experiments on ion S have suggested the formation of a covalent Si-C bond in an addition product that subsequently evolves by loss of C<sub>3</sub>H<sub>6</sub>. However, CID is not structurally diagnostic for simple alkylsilyl cations [69] and any characterization using this tool was not further attempted. Ion-molecule reactions appear as more selective probes for structural elucidation. In particular, one may rely on the well established notion that cations in which the positive charge is borne by the silicon atom are powerful electrophiles and tend to form strong covalent bonds with various compounds containing electronegative atoms including water, alcohols and amines [70]. Accordingly, potentially diagnostic reagents have been sought in the ROR' class of compounds (R,R' = H,H; i-C<sub>3</sub>H<sub>7</sub>,H; t-C<sub>4</sub>H<sub>9</sub>,CH<sub>3</sub>), though preliminary experiments were run to explore also the reactivity toward alkyl chlorides such as  $C_3H_5Cl$  and  $t-C_4H_9Cl$ . The reactions of both the sample ion **S** and the model ions (**2**,**3**,**4**,**6**) have been studied by allowing the ions formed in the external ions source to react with the neutral present in the FT-ICR cell at a controlled pressure value in the range of  $10^{-8}$ – $10^{-7}$  mbar.



**Fig. 1.** Time dependence of the relative ion abundances (1%) when selected model ions **3** (**■**) at m/z 99 from Cl(C<sub>3</sub>H<sub>8</sub>) of allyltrimethylsilane, are allowed to react with H<sub>2</sub>O at  $1.5 \times 10^{-8}$  mbar. Product ions are formed at m/z 75 ( $\blacklozenge$ ).

The reaction with water leads to a unique product ion of  $C_2H_7SiO^+$  composition, likely corresponding to  $(CH_3)_2SiOH^+$  [Eq. (3)].

$$C_5H_{11}Si^+ + H_2O \rightarrow C_2H_7SiO^+ + [C_3H_6]$$
 (3)

An exemplary plot of the time dependence of ion abundances is reported in Fig. 1, illustrating the reaction of model ion **3**, from  $Cl(C_3H_8)$  of allyltrimethylsilane. The second order rate constants were obtained from kinetics run at three or more different values of the H<sub>2</sub>O pressure and found to yield the same value within experimental error. The results are listed in Table 1 showing that  $C_5H_{11}Si^+$  ions display the same reactivity with water, irrespective of their origin. This reagent is therefore unsuitable to discriminate among the different structures of the model ions.

The reaction of  $C_5H_{11}Si^+$  ions with *i*- $C_3H_7OH$  proceeds along two competing pathways leading to  $C_2H_7SiO^+$  (likely corresponding to  $(CH_3)_2SiOH^+$ ) and to  $C_5H_{13}SiO^+$  (which may be assigned to *i*- $C_3H_7OSi(CH_3)_2^+$ ) [Eq. (4a) and (4b)]. In the presence of *i*- $C_3H_7OH$ ,  $(CH_3)_2SiOH^+$  ions react further to give  $(CH_3)_2Si(OH)(OH_2)^+$  and *i*- $C_3H_7OSi(CH_3)_2(OH_2)^+$  as the plausible products at *m*/*z* 93 and *m*/*z* 135 from two subsequent reaction steps. An exemplary kinetic run is shown in Fig. 2 illustrating the relative ion abundances for the reaction of model ion **2**, from Cl( $C_3H_8$ ) of (Z)-1-(trimethylsilyl)propene, with *i*- $C_3H_7OH$ . The kinetic results obtained at different values of the neutral pressure were averaged and are listed in Table 1.

#### Table 1

Kinetic data for the gas phase reaction of  $C_5H_{11}Si^+$  ions with ROR' nucleophiles.

Precursor of reactant ion <sup>a</sup>	ROR'	$k_{exp}^{b}$	$\Phi^{c}$
(Z)-1-(Trimethylsilyl)propene (2) (E)-1-(Trimethylsilyl)propene (4) 2-(Trimethylsilyl)propene (6) Allyltrimethylsilane (3) S	$H_2O$ $H_2O$ $H_2O$ $H_2O$ $H_2O$ $H_2O$	$\begin{array}{c} 2.2 \pm 0.8 \\ 2.1 \pm 1.2 \\ 2.0 \pm 1.3 \\ 2.3 \pm 0.5 \\ 2.0 \pm 0.6 \end{array}$	$\begin{array}{c} 12 \pm 4 \\ 12 \pm 6 \\ 11 \pm 7 \\ 13 \pm 3 \\ 11 \pm 3 \end{array}$
(Z)-1-(Trimethylsilyl)propene ( <b>2</b> ) (E)-1-(Trimethylsilyl)propene ( <b>4</b> ) 2-(Trimethylsilyl)propene ( <b>6</b> ) Allyltrimethylsilane ( <b>3</b> ) <b>S</b>	i-C <sub>3</sub> H <sub>7</sub> OH i-C <sub>3</sub> H <sub>7</sub> OH i-C <sub>3</sub> H <sub>7</sub> OH i-C <sub>3</sub> H <sub>7</sub> OH i-C <sub>3</sub> H <sub>7</sub> OH	$\begin{array}{l} 4.5 \pm 1.5 \\ 5.3 \pm 0.5 \\ 6.0 \pm 1.5 \\ 4.1 \pm 0.2 \\ 5.3 \pm 1.2 \end{array}$	$\begin{array}{c} 29 \pm 10 \\ 34 \pm 3 \\ 40 \pm 10 \\ 26 \pm 2 \\ 34 \pm 4 \end{array}$
S	t-C₄H9OCH3	$7.6 \pm 0.8$	$49\pm 5$

<sup>a</sup> Reactant ion designated in parentheses.

 $^{\rm b}\,$  Second order rate constant in units of  $10^{-10}\,cm^3\,molecule^{-1}\,s^{-1},$  at 300 K.

<sup>c</sup> Reaction efficiency =  $k_{exp}/k_{coll}$ , expressed as percentage.



**Fig. 2.** Time dependence of the relative ion abundances (l%) when selected model ions **2** ( $\blacktriangle$ ) at m/z 99 from Cl(C<sub>3</sub>H<sub>8</sub>) of (Z)-1-(trimethylsilyl)propene, are allowed to react with i-C<sub>3</sub>H<sub>7</sub>OH at 4.3 × 10<sup>-8</sup> mbar. Primary product ions are formed at m/z 75 ( $\blacklozenge$ ) and m/z 117 (×). Secondary product ions are at m/z 93 ( $\blacksquare$ ) and m/z 135 (\*).

Table 2

Product ratios for the gas phase reaction of C<sub>5</sub>H<sub>11</sub>Si<sup>+</sup> ions with ROR' nucleophiles.

Precursor of reactant ion <sup>a</sup>	ROR'	$P_1/P_2^{b}$
(Z)-1-(Trimethylsilyl)propene (2) (E)-1-(Trimethylsilyl)propene (4) 2-(Trimethylsilyl)propene (6) Allyltrimethylsilane (3) S	i-C <sub>3</sub> H <sub>7</sub> OH i-C <sub>3</sub> H <sub>7</sub> OH i-C <sub>3</sub> H <sub>7</sub> OH i-C <sub>3</sub> H <sub>7</sub> OH i-C <sub>3</sub> H <sub>7</sub> OH	$\begin{array}{c} 8.5 \pm 1.7^c \\ 11 \pm 1.8^c \\ 20 \pm 5^c \\ 4.3 \pm 0.5^c \\ 21 \pm 2^c \end{array}$
(Z)-1-(Trimethylsilyl)propene ( <b>2</b> ) (E)-1-(Trimethylsilyl)propene ( <b>4</b> ) 2-(Trimethylsilyl)propene ( <b>6</b> ) Allyltrimethylsilane ( <b>3</b> ) <b>S</b>	t-C4H9OCH3 t-C4H9OCH3 t-C4H9OCH3 t-C4H9OCH3 t-C4H9OCH3 t-C4H9OCH3	$\begin{array}{c} 2.6 \pm 0.3^{d} \\ 2.5 \pm 0.3^{d} \\ 4.6 \pm 0.7^{d} \\ 24 \pm 5^{d} \\ 4.1 \pm 0.7^{d} \end{array}$

<sup>a</sup> Reactant ion designated in parentheses.

 $^{\rm b}$  Ratio of the yields of product ions  $P_1$  and  $P_2$  obtained from the ion-molecule reactions run at 300 K.

<sup>c</sup>  $P_1 = C_2 H_7 SiO^+$  and  $P_2 = C_5 H_{13} SiO^+$ .

<sup>d</sup>  $P_1 = C_3 H_9 SiO^+$  and  $P_2 = C_6 H_{15} SiO^+$ .

$$C_5H_{11}Si^+ + i-C_3H_7OH \longrightarrow C_2H_7SiO^+ + [C_6H_{12}]$$
 (4a)  
 $C_5H_{13}SiO^+ + [C_3H_6]$  (4b)

As expected from a nucleophile stronger than water, the reaction efficiencies are higher, their values comprised within 26–40%, and do not lend a useful tool to distinguish among isomeric structures. The branching between the two reaction channels 4a and 4b appears more informative and is extracted by extrapolating the relative ion yields to initial time. The formation of  $C_2H_7SiO^+$  is always favored with respect to  $C_5H_{13}SiO^+$  but the branching ratio is different for the various isomers ranging from 4.3 to 21 (Table 2). Thus, while the  $C_5H_{11}Si^+$  ions deriving from (*Z*)- and (*E*)-1-(trimethylsilyl)propene showing ratios of 8.5 and 11, respectively, are not clearly discriminated, the observed value of 21 for the sample ion **S** is quite close to the value for the model ion **G** from CI( $C_3H_8$ ) of 2-(trimethylsilyl)propene and is far from the ratio of 4.3 displayed by the model ion **3** from allyltrimethylsilane.

In a further effort to obtain safer support for a structural assignment, the reactivity pattern toward *tert*-butyl methyl ether  $(t-C_4H_9OCH_3)$  has been examined. When  $C_5H_{11}Si^+$  ions are allowed to react with  $t-C_4H_9OCH_3$  three primary product ions are observed, namely  $C_6H_{15}SiO^+$ ,  $C_3H_9SiO^+$ , and  $C_4H_9^+$ , as shown in Eq. (5). The plausible composition of  $C_6H_{15}SiO^+$ ,  $C_3H_9OSi(CH_3)_2^+$ ,  $CH_3OSi(CH_3)_2^+$ , and  $t-C_4H_9^+$ , respectively.

$$C_6 H_{15} SiO + [C_4 H_8]$$
(5a)

$$C_{5}H_{11}Si^{+} + t - C_{4}H_{9}OCH_{3} \longrightarrow C_{3}H_{9}SiO^{+} + [C_{7}H_{14}]$$
(5b)

$$\longrightarrow C_4 H_9^+ + [C_5 H_{11} SiOC H_3]$$
 (5c)

The exemplary plot of Fig. 3 shows the kinetic progress of the reaction of the sample ion **S** from the addition of  $(CH_3)_3Si^+$  to acetylene. As in the case of the nucleophiles  $H_2O$  and  $i-C_3H_7OH$ , the evaluation of the efficiency for the reactions of the model ions does not appear to yield distinct values that could be used for any reliable structural assignment and further efforts to collect these data were not engaged. Given the higher nucleophilicity of  $t-C_4H_9OCH_3$  also the reaction efficiency is higher, on the order of 50%, and the value for the reaction of **S** is reported in Table 1.

As observed for the reaction with *i*-C<sub>3</sub>H<sub>7</sub>OH as probe nucleophile, it is the branching ratio into the different product channels that is most revealing about structural differences in the model ions. The branching ratio into the C<sub>3</sub>H<sub>9</sub>SiO<sup>+</sup> and C<sub>6</sub>H<sub>15</sub>SiO<sup>+</sup> product ions is found to be the most informative.

The third product ion,  $C_4H_9^+$ , is however interfering due to a proton transfer reaction to  $t-C_4H_9OCH_3$  which forms a cation  $(C_5H_{13}O^+)$  formally isobaric with  $C_3H_9SiO^+$ . The high resolving power of the FT-ICR mass spectrometer has permitted to solve the problem by the distinct separation of the two ion signals at m/z $89.0961(C_5H_{13}O^+)$  and m/z 89.0417 ( $C_3H_9SiO^+$ ). The values of the branching ratios gained by the correct evaluation of the relative abundance of the  $C_3H_9SiO^+$  species is reported in Table 2.

The relative abundances of  $C_3H_9SiO^+$  and  $C_6H_{15}SiO^+$  product ions are fairly constant with respect to reaction time (though only the early part of the kinetic progress of the reaction was considered) and neutral pressure. The data collected in Table 2 indicate that the reactivity behavior of the sampled ion population S conforms to the one displayed by the model ion **6** from 2-(trimethylsilyl)propene. The partition into the C<sub>2</sub>H<sub>7</sub>SiO<sup>+</sup> and C<sub>5</sub>H<sub>13</sub>SiO<sup>+</sup> products of the reaction with i-C<sub>3</sub>H<sub>7</sub>OH is 20±5 from the model ion and  $21\pm2$  from **S**. The two values are equal within experimental error and so are the corresponding ratios for the formation of  $C_3H_9SiO^+$  and  $C_6H_{15}SiO^+$  product ions,  $4.6\pm0.7$  and  $4.1\pm0.7$ , respectively, from the reaction with  $t-C_4H_9OCH_3$ . The results of the ion-molecule reactions clearly suggest that the C<sub>5</sub>H<sub>11</sub>Si<sup>+</sup> addition product from the (CH<sub>3</sub>)<sub>3</sub>Si<sup>+</sup> reaction with acetylene should be ascribed the structure of 2-propenyl-dimethylsilyl cation 6 [Eq. (6)].



## 3.3. $C_5H_{11}Si^+$ isomers and rearrangement pathways: a quantum chemical assay

The rearrangement reaction depicted in Eq. (6) involves a complex pathway that is conceivably initiated after the formation of a nascent  $(CH_3)_3Si^+$ -acetylene complex. This adduct seemingly undergoes at least a 1,2-methyl migration from Si to C and a 1,2-H shift process. The driving force of the reaction lies in the formation of an ion where the positive charge is formally placed on silicon but the involvement of activation barriers is underlined by the reactivity behavior observed at higher pressure (3 mbar to 1 atmosphere), where the isomerization does not take place. In order to elucidate the relative energies of the various ionic intermediates and the energy profile of the plausible paths linking them, *ab initio* 



**Fig. 3.** Time dependence of the relative ion abundances (*I*%) when selected sample ions **S** at *m*/*z* 99 from the addition of (CH<sub>3</sub>)<sub>3</sub>Si<sup>+</sup> to acetylene ( $\blacktriangle$ ) are allowed to react with *t*-C<sub>4</sub>H<sub>9</sub>OCH<sub>3</sub> at 1.9 × 10<sup>-8</sup> mbar. Primary product ions are formed at *m*/*z* 131 ( $\Box$ ) (C<sub>6</sub>H<sub>15</sub>SiO<sup>+</sup>), *m*/*z* 89 (**■**) (C<sub>3</sub>H<sub>9</sub>SiO<sup>+</sup>), and *m*/*z* 57 ( $\blacklozenge$ ) (C<sub>4</sub>H<sub>9</sub><sup>+</sup>). Secondary product ions are at *m*/*z* 89 (**●**) (C<sub>5</sub>H<sub>13</sub>O<sup>+</sup>), and *m*/*z* 121 (+).

calculations at the CCSD(T)/6-311++G(2d,2p)//B3LYP/6-311G(2d,p) level of theory were undertaken whose results are summarized. The significant structures that were investigated include the isomers depicted in Chart 1 together with the nascent (CH<sub>3</sub>)<sub>3</sub>Si<sup>+</sup>-acetylene complex **1**, formerly described by the limiting geometries **1A** and **1B**.

Fig. 4 illustrates the optimized geometries of the stable isomers and the transition states for the rearrangement paths obtained by B3LYP/6-311G(2d,p) calculations. Table S1 in the supplementary data summarizes the computational data obtained at both B3LYP/6-311G(2d,p) and CCSD(T)/6-311++G(2d,2p)//B3LYP/6-311G(2d,p) level about all relevant species that have been examined and Table S2 provide the Cartesian coordinates of the optimized structures.

Because silvl substituted vinyl cations are known to be quite flexible and the obtained structures may be dependent on the chosen method, also MP2 computations have been applied to optimize few significant species and check whether significantly different structures were obtained. To this purpose geometry optimization and frequency analysis at MP2/6-311G(2d,p) level of theory have been performed on species 1,2,5,6, TS<sub>12</sub> and TS<sub>15</sub>. The so-obtained thermodynamic data are listed in Table S3. Table S4 provides the Cartesian coordinates of the optimized structures. Table S5 presents a comparison of selected geometrical parameters evaluated by the B3LYP and MP2 methods. The MP2 results do not present significant differences with respect to the corresponding structures optimized at B3LYP/6-311G(2d,p) level. In view of the substantial consistency of B3LYP/6-311G(2d,p) and MP2/6-311G(2d,p) computational results, the forthcoming discussion will refer to the final data computed at CCSD(T)/6-311++G(2d,2p)//B3LYP/6-311G(2d,p) level.

As shown by the results collected in Fig. 4, ion **4** is the most stable species among all  $C_5H_{11}S^{i+}$  ions that were examined, while the  $(CH_3)_3S^{i+}$ -acetylene complex **1**, showing an optimized geometry in between the limiting structures **1A** and **1B**, is 95 kJ mol<sup>-1</sup> higher in energy. Complex **1** is endowed with a highly fluxional structure. In fact, the displacement of the silyl group between the two C-atoms in two equivalent geometries occurs via a  $C_s$  transition state that is about 1 kJ mol<sup>-1</sup> less stable than **1**.

To explore the relevant sections of the potential energy surface whereby the conceivable rearrangements of  $C_5H_{11}Si^+$  ions can take place, several paths have been explored. Eq. (7) shows the rearrangement of **1** to ion **2** involving the migration of a methyl



**Fig. 4.** Geometries of  $C_5H_{11}Si^+$  isomers and of the transition states linking them, obtained by B3LYP/6-311G(2d,p) computations. Relative energies are reported in kJ mol<sup>-1</sup> (in parentheses, see Table S1).

group from silicon to carbon (transition state **TS**<sub>12</sub>). The arrows in Eq. (7) point out the motion of the CH<sub>3</sub> group and the rotation around the double bond. The product ion **2** is the second most stable species but the isomerization to **4**, representing the most stable among the investigated structures, requires a  $(Z) \rightarrow (E)$ rearrangement (transition state **TS**<sub>24</sub>). may then undergo electrocyclic ring opening to give **4**. However, the candidate 2-silacyclopropyl intermediate does not represent a local minimum evolving into structure **6** upon geometry optimization.



In a similar way, the formation of isomer **6** is depicted in Eq. (8). The process starts from **1** and proceeds by a 1,2-H shift to form an intermediate  $\alpha$ -silyl vinyl cation **5** (transition state **TS**<sub>15</sub>). A 1,2-shift of a methyl group from Si to C leads from **5** to ion **6** holding the positive charge on silicon (transition state **TS**<sub>56</sub>). From ion **6** a rearrangement process can be conceived involving both a 1,2-shift of (CH<sub>3</sub>)<sub>2</sub>Si and a 1,2-shift of a hydrogen atom to give the most stable isomer **4** (transition state **TS**<sub>46</sub>), as shown in Eq. (9). In this equation, and in the following ones, the arrows point out the migration of an atom or group. Alternatively, a stepwise path for the **6** to **4** rearrangement has been taken into consideration involving an intermediate 2-silacyclopropyl cation which



A pathway may be further envisioned leading to the allyldimethylsilyl cation **3**, whose formation derives from ions

(9)



**Fig. 5.** Energy profiles of the proposed pathways following the  $(CH_3)_3Si^+$  addition to acetylene evaluated at CCSD(T)/6-311++G(2d,2p)//B3LYP/6-311G(2d,p) level of theory. Values of  $E_{rel}$  at 0 K are given in kJ mol<sup>-1</sup>.

2/4 by a formal 1,3-H shift (transition states  $TS_{23}$  and  $TS_{34}$ , respectively), as shown in Eq. (10).



The energy profile of the various paths that were envisioned is illustrated in Fig. 5, showing the relative energies of the significant species evaluated at CCSD(T)/6-311++G(2d,2p)//B3LYP/6-311G(2d,p) level of theory. Throughout the diagram a broken line marks the energy content of the separated (CH<sub>3</sub>)<sub>3</sub>Si<sup>+</sup>-acetylene molecules combining to form complex 1 that is stabilized by 91 kJ mol<sup>-1</sup> relative to the free reagents. The reaction exothermicity, however, remains stored in the adduct ion 1 unless dissipated by radiative emission or energy transfer by unreactive collisions with a bath gas. Both processes are inefficient for a relatively small species in a highly dilute environment [58,59] so that the energy released in the addition process contributes to form a 'hot' species that can undergo rearrangement processes involving substantial activation barriers [Eq. (2)]. The plot shows that the transition state lying lowest in energy, TS<sub>15</sub>, allows the conversion of 1 to 5. Ion 5 is probably a fleeting intermediate because it can proceed without any appreciable activation barrier to form 6. Ion 6 is likely to represent a dead end product under the prevailing experimental conditions.

A further rearrangement to the most stable species **4** requires passing an activation barrier that protrudes above the energy content of the reactant pair so that the corresponding transition state **TS<sub>46</sub>** is hardly accessible. The **TS<sub>46</sub>** transition state combines a 1,2-H shift with a 1,2-(CH<sub>3</sub>)<sub>2</sub>Si shift involving the same two C-atoms, though in opposite direction [Eq. (9)]. The reaction path allowing the conversion of **1** into **2** could also be accessed because the corresponding transition state, **TS<sub>12</sub>**, lies only slightly higher in energy (by ca. 6 kJ mol<sup>-1</sup>) than the separated (CH<sub>3</sub>)<sub>3</sub>Si<sup>+</sup>-acetylene couple. It could provide a route to isomer **4**, if a (Z)  $\rightarrow$  (E) isomerization were further allowed. However, not only is the latter process inhibited by a transition state placed above the reference level, but also the formation of **2** in any significant amount is rather disproven by the gathered experimental evidence. The lack of any evidence suggesting the presence of the allyl-substituted silyl cation **3** is amply justified by the high energy barrier associated to the 1,3-H shift linking **3** to the (E)/(Z) isomers **2** and **4** by way of **TS**<sub>23</sub> and **TS**<sub>34</sub>. The high barriers computed for the 1,3-H shifts are indeed what is expected for this rearrangement in allylic systems on the basis of FMO theory. It may further be noted that the reference species **2,3,4,6** do indeed retain the original structure from each individual precursor because of the high activation barriers for their interconversion, as testified by the computed energy profiles.

#### 4. Conclusion

The neat process of (CH<sub>3</sub>)<sub>3</sub>Si<sup>+</sup> addition to acetylene can only be examined in the gas phase where the CI(CH<sub>4</sub>) of (CH<sub>3</sub>)<sub>4</sub>Si provides an entry to naked (CH<sub>3</sub>)<sub>3</sub>Si<sup>+</sup> ions in a dilute environment lacking potential nucleophiles that tend to trap this highly electrophilic species, masking its intrinsic reactivity. Though seemingly simple, the (CH<sub>3</sub>)<sub>3</sub>Si<sup>+</sup> addition to acetylene is a complex process when examined at low pressure in the  $10^{-8}$ – $10^{-7}$  mbar range of FT-ICR mass spectrometry. The formation of formal adduct ions, C5H11Si<sup>+</sup>, reveals the occurrence of a rearrangement process allowed by the excess internal energy released in the primary addition of (CH<sub>3</sub>)<sub>3</sub>Si<sup>+</sup> to acetylene. The structure of C<sub>5</sub>H<sub>11</sub>Si<sup>+</sup> ions has been probed by ionmolecule reactions, taking advantage of the temporal resolution allowing kinetic determinations and also of the mass resolution which permitted to discriminate formally isobaric product ions. When confronted with the reactivity pattern of model ions, the sampled  $C_5H_{11}Si^+$  adducts, ions **S**, are found to behave in a quite similar way as the 2-propenyl-dimethylsilyl cation 6. Additionally, the partition in competing paths following the reaction with selected neutrals (i-C<sub>3</sub>H<sub>7</sub>OH and t-C<sub>4</sub>H<sub>9</sub>OCH<sub>3</sub>) is different when other stable isomers (2,3,4) are tested. The structural assignment of the observed C<sub>5</sub>H<sub>11</sub>Si<sup>+</sup> adducts, allowed by the distinct ionmolecule reactivity, is further supported by the quantum chemical calculations of the potential isomers and the related energy profiles for their interconversion pathways. The computational results confirm the experimental findings. The nascent (CH<sub>3</sub>)<sub>3</sub>Si<sup>+</sup>-acetylene complex 1 may rearrange to isomer 6 passing the lowest activation energy barrier associated to a 1,2-H shift from  $C_{\alpha}$  to  $C_{\beta}$  of the former acetylene unit. The so-formed  $\alpha$ -silvl vinyl cation **5** is a transient intermediate that can proceed to 6 in a nearly barrierless process involving a Si to C methyl migration and forming a stable species with a positive charge centered on silicon. Further rearrangements to other isomers including the most stable one, 4, is inhibited by activation energy barriers protruding above the energy level of the reactant pair. An alternative path energetically accessible, namely  $1 \rightarrow 2$ , is associated to an activation energy barrier of ca. 97 kJ mol<sup>-1</sup>. This rearrangement does not appear to take place, though, suggesting that the differential energy barrier of ca.  $35 \text{ kJ} \text{ mol}^{-1}$  relative to  $1 \rightarrow 6$  is effective in rendering the reaction selective. At the same time, the  $1 \rightarrow 6$  rearrangement is hampered by the collisional relaxation occurring at 3-5 mbar in HPMS where adventitious water is a final trap for (CH<sub>3</sub>)<sub>3</sub>Si<sup>+</sup> ions whereas 1 is efficiently stabilized at atmospheric pressure where it ultimately undergoes deprotonation to the neutral substitution product, (CH<sub>3</sub>)<sub>3</sub>SiC=CH. In conclusion, the integrated approach combining bimolecular ion-chemistry with quantum chemical calculations has provided a consistent view of the reactivity going on in (CH<sub>3</sub>)<sub>3</sub>Si<sup>+</sup>-acetylene adducts in gaseous environments at widely different pressures. In this context, it is interesting to compare the behavior of the gaseous  $(CH_3)_3Si^+$ -acetylene complex with a related system that has been recently investigated using matrix isolation IR spectroscopy and quantum chemical calculations [71]. Trimethylsilylacetylenes ((CH<sub>3</sub>)<sub>3</sub>SiC=CR, R = H, CH<sub>3</sub>, Si(CH<sub>3</sub>)<sub>3</sub>) have been codeposited with SbF5 and submitted to vibrational analysis after deposition and upon warming of the matrix. New bands appearing in the 1600 cm<sup>-1</sup> spectral region have been assigned to silaallylcations such as 2 and 6 suggested to arise by protonation and ensuing isomerization processes. Vibrational spectroscopy of the gaseous sample ion **S** using IR multiple photon dissociation spectroscopy [72,73] is a forthcoming effort to settle the significant features of the potential energy surface of gaseous C<sub>5</sub>H<sub>11</sub>Si<sup>+</sup> ions.

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#### Appendix A. Supplementary data

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