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Silylium ions †

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Abstract. The history and state of the art of research on silylium ions are summarised. Achievements of the last two decades in the preparation of silylium ions as individual species in solutions and crystals and as intermediates in reactions of organosilicon compounds are considered. Attention is focused on ion-molecular reactions of silylium ions with nucleophilic reagents in the gas and condensed phases. The bibliography includes 164 references.

I. Introduction

For more than five decades, scientists have debated whether silicon compounds can exhibit chemical properties characteristic of their carbon analogues. Since silicon and carbon are both Group 14 elements, attempts were made to find features of organosilicon chemistry characteristic of organic chemistry, *e.g.*, the ability of Si atoms to be involved in formation of Si = E double bonds (E = Si, C, O, N, *etc.*), long-chain silicon polymers and intermediates analogous to carbon compounds (for example, to carbenes and carbocations). Available experimental data show that the chemical properties of carbon are very different from those of silicon. First and foremost, silicon compounds containing multiple bonds are very unstable (unlike carbon analogues). Up to the mid-twentieth century, the existence of such compounds has been doubted.[1] First publications on the synthesis of unstable silicon compounds containing Si = Si, Si = C, *etc.* bonds date back to 1967.[2–7] Nowadays, the opinion that silicon cannot form multiple bonds is completely disproved.[8,9] The formation of polysilanes, whose properties have long been poorly known, was also proved.[10,11] However, the existence of silicon intermediates analogous to carbon intermediates is still an open question. In recent years, silylenes,[12–14] which are silicon analogues of well-known carbenes,[15] have been synthesised and their properties have been studied. However, it appeared to be very difficult to obtain (particularly, in the condensed phase) the tricoordinate organosilicon cations R_3Si^+ analogous to the carbocations R_3C^+ and prove their existence. Earlier, silylium ions in the gas phase have been studied primarily by ion cyclotron resonance and conventional mass spectrometry.[16] However, the applicability of these methods is limited to observations of charged particles in a rarefied-gas atmosphere.

The present review deals with silylium ions and summarises both the history and state of the art of research in this field. The review covers the achievements of the last two decades in the synthesis of silylium ions as individual species both in solutions and crystals and as intermediates in reactions of organosilicon compounds. Emphasis is given to the reactivity of silylium ions and their ion-molecular reactions with nucleophilic reagents in the gas and condensed phases, which have remained virtually unknown until recently. It should be noted that in Russia the latest review of research into silylium ions was published by Nefedov *et al.*[17] in 1986. Data on the synthesis and results of studies of silylium ions in the gas and condensed phases have been partially systematised.[18–20] In addition, certain aspects of this problem have been summarised in short publications.[21,22] The aim of the present review is to provide a deep insight into the development of chemistry of silylium ions.

II. History of investigations into silylium ions

The discovery of carbenium ions R_3C^+ isoelectronic with the silylium ions R_3Si^+ has played a great role in the development of organic chemistry because most organic reactions proceed *via* these reactive intermediates.[23] Their existence was established in the early twentieth century (see, for example, Ref. 24). For almost a century, these intermediates have attracted the most attention in studies of mechanisms of various chemical processes. In the 1990s, researchers have shifted their interest to the related species, *viz.*, silylium ions.

The ways of development of the chemistry of organosilicon cations R_3Si^+ and their carbon analogues R_3C^+ are substantially different. Even the name of the R_3Si^+ cation has long been debated. At different times, this cation was referred to as the siliconium,[25] silycenium [26] or silylenium [27] cation. Nowadays, it is called the silylium ion.[28] Taking into account that the carbenium ions are of tremendous importance in organic chemistry, the formation of silylium ions as intermediates in many organosilicon

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† According to the latest IUPAC recommendations, the tricoordinate R_3Si^+ cation is called the silylium ion.

reactions was often postulated without proof. However, alternative mechanisms can, as a rule, be suggested for such reactions.

The possible involvement of silylium ions as intermediates in reactions has been reported for the first time by Whitmore and Sommer,[25] who studied the rearrangement of chloromethyltrimethylsilane under the action of $AlCl_3$.

$$Me_3SiCH_2Cl \xrightarrow{AlCl_3} [Me_3Si{-}CH_2]^+AlCl_4^- \xrightarrow{\sim Me} \longrightarrow [Me_2Si^+CH_2Me]AlCl_4^- \longrightarrow Me_2Si(Cl)Et$$

The formation of silylium ions as reactive intermediates was also postulated in the rearrangement of (1-haloalkyl)trimethylsilanes in the presence of SbF_5 (see Ref. 29) and in the rearrangement of (1-hydroxyalkyl)trimethylsilanes in the presence of BF_3.[30] The ionic mechanism was proposed without proof to account for the so-called β-cleavage of trialkyl(2-haloethyl)silanes **1** in the presence of $AlCl_3$ [31] or in an aqueous ethanolic medium.[32] These reactions afford trialkylchlorosilanes **2** or trialkylethoxysilanes **3**.

$$R_3SiCH_2CH_2Cl \xrightarrow{AlCl_3} [R_3SiCH_2CH_2]^+AlCl_4^- \xrightarrow{-CH_2=CH_2}$$

1

$$\longrightarrow [R_3Si]^+AlCl_4^- \longrightarrow R_3SiCl + AlCl_3$$

2

$$R_3SiCH_2CH_2Cl \xrightarrow{EtOH,\ H_2O} [R_3SiCH_2CH_2]^+Cl^- \xrightarrow{-CH_2=CH_2}$$

1

$$\longrightarrow [R_3Si]^+Cl^- \xrightarrow{EtOH} R_3SiOEt + HCl$$

3

R = Alk.

Dolgov *et al.*[33,34] studied disproportionation of dialkylchlorosilanes **4** and also suggested that this reaction proceeds by the ionic mechanism.

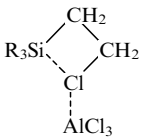
$$R_2SiHCl \xrightarrow{AlCl_3} [R_2SiH]^+AlCl_4^- \xrightarrow[-R_2SiH_2]{4}$$

4

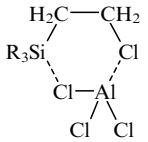
$$\longrightarrow [R_2SiCl]^+AlCl_4^- \longrightarrow R_2SiCl_2 + AlCl_3$$

In this case, no experimental evidence for the proposed reaction mechanism was reported as well.

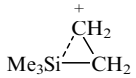
Alternative mechanisms of the above-considered reactions involve the intermediate formation of a four- (structure **5a**) or six-centred (**5b**) activated complex[35] and a non-classical carbenium ion **5c**.[36]



5a



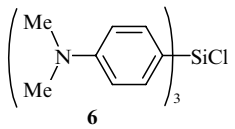
5b



5c

It is noteworthy that the rearrangement of fluorodiethylsilane occurs spontaneously in the absence of catalysts,[37] which suggests that this reaction proceeds through a cyclic transition state of type **5c**.

Many researchers attempted to prepare and characterise stable silylium ions isostructural with carbenium ions in the condensed phase. A silicon analogue of ionic tris(*p*-dimethylaminophenyl)chloromethane, *viz.*, silyl chloride **6**, was synthesised.[38,39]



6

However, studies by physicochemical methods (conductometry, IR and UV spectroscopy, X-ray diffraction analysis, *etc.*) demonstrated that compound **6** is covalent. Silicon perchlorates R_3SiClO_4 (R = Alk) were demonstrated[40] to be covalent, unlike ionic crystalline triarylmethyl perchlorates.

Olah *et al.*[26,41] attempted to synthesise classical silylium ions in a superacidic medium ($FSO_3H-SbF_5-SO_2$ system) of extremely low nucleophilicity. Under these conditions, non-primary carbenium cations are stable and are generated from various organic compounds.[42] In this medium, the behaviour of trialkylalkoxysilanes **3** was studied by low-temperature NMR spectroscopy. It was found that these compounds initially undergo protonation followed by the replacement giving rise to trialkylfluorosilane.

$$R_3SiOMe \xrightarrow{FSO_3H-SbF_5-SO_2} \left[R_3Si{-}\overset{+}{O}(H){-}Me\right] \xrightarrow[-30\ ^\circ C]{F^-} R_3SiF + MeOH$$

3

R = Alk.

In this process, no R_3Si^+ ions were detected. The formation of trialkylfluorosilanes was accounted for by the formation of a pentacovalent intermediate **7** (for R = Me).[41]

$$\left[Me_3Si{-}\overset{+}{O}(H){-}Me\right] \xrightarrow{F^-} \left[F{-}Si^-(Me)_2{-}\overset{+}{O}(H){-}Me\right] \xrightarrow[-MeOH]{} Me_3SiF$$

7

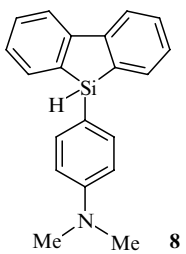
Analogous results were obtained upon storage of hexaalkyldisiloxanes in a superacidic medium.[41]

One of the main problems in preparing silylium ions in the condensed phase is associated with the nature of the leaving group. In organic chemistry, carbenium ions are traditionally generated by the S_N1 or E1 mechanisms, a halogen- (I^-, Cl^-, *etc.*) or oxygen-containing anion serving, as a rule, as the leaving group. Taking into account high strength of the silicon bonds with halogens and oxygen, the latter cannot be used as the leaving groups for generation of silylium ions. Corey[43] described the synthesis of silylium ions by reaction (1) with the use of the hydride ion as the leaving group.

$$[Ph_3C]^+ClO_4^- + R_3SiH \longrightarrow Ph_3CH + [R_3Si]^+ClO_4^- \qquad (1)$$

Actually, the Si–H bond is weaker than the C–H bond and, consequently, reaction (1) is thermodynamically favourable. This reaction is named after Corey and it has been used for years to prove the formation of silylium ions as stable species and short-lived intermediates in various transformations.

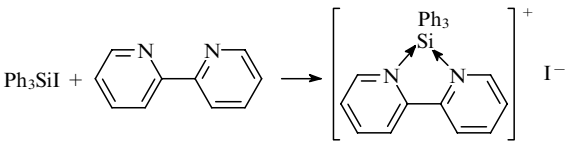
In 1975, the synthesis of stable silylium ions as a result of hydride ion abstraction from compound **8** was documented.[44,45]



8

However, these results were later rejected.[27, 46] These studies ended in failure apparently because the researchers assumed that the properties of silicon are completely analogous to those of carbon.

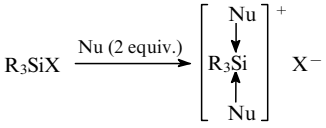
In the study,[47] the authors succeeded in preparing positively charged organosilicon ions by coordination of silicon with compounds having a basic character. For example, the reaction of iodotriphenylsilane with 2,2′-bipyridine gave salt **9** with a pentacovalent silicon ion.



9

More recently, other analogous pentacovalent cations were prepared.[48, 49]

In the review,[18] which summarises the results of research on silylium ions obtained by that time, a conclusion was drawn that positively charged organosilicon ions can be generated only as a result of the nucleophilic attack on the Si atom.



R = Alk, Ar; X is a halogen; Nu is a nucleophile.

However, it should be emphasised that the pentacoordinate ion thus produced differs in principle from the trivalent silylium ion R_3Si^+. The latter, like the carbenium ion, could be formed upon the heterolytic cleavage of the Si–X bond.

Although the attempts to detect the silylium ions R_3Si^+ in condensed phases failed, these species were reliably identified in rarefied gases. Taking into account that the physical properties of silicon (thermodynamic, electronic, *etc*.) should make the generation of silylium ions easier compared to the structurally similar carbenium ions, the reasonable question arises as to why this process is hindered in the condensed phase?

The answer to this question can be found by analysing the results of quantum-chemical studies,[50] which confirm a substantial difference in the chemical properties of carbon and silicon. First and foremost, this refers to the unique ability of the silicon atom to increase its coordination number. For example, compounds with the hypercoordinate silicon atom (for example, the SiF_6^{2-} anion) are well known, whereas analogous carbon compounds are absent. Due to the ability of silicon to have high coordination numbers, silylium ions, unlike carbocations, are more prone to complexation with various nucleophiles, including counterions and solvents used in the synthesis of organosilicon compounds. Apparently, this is responsible for the fact that all attempts to observe silylium ions in solution failed.

The above facts argue against the conclusion[18] that it is impossible to prepare the trivalent silylium ions R_3Si^+ in the condensed state; that is, a different in principle strategy is required for their generation.

III. State of the art of research on silylium ions

1. Silylium ions in the gas phase

The existence of silylium ions in the gas phase is beyond doubt. These ions are easily generated in rarefied gases by various methods, including electron impact, photoionisation and chemical ionisation. The appearance potentials of silylium ions are substantially lower than those of carbenium ions.[51] Taking into account that, until recently, virtually all attempts to generate and characterise silylium ions in the condensed phase failed, any information on these ions obtained in gas-phase studies is of considerable importance and is very useful. Not only thermodynamic but also certain physical characteristics of silylium ions were determined. In particular, studies of the H_3Si^+ ion by gas-phase infrared laser spectroscopy demonstrated[52] that this cation (like the H_3C^+ ion) is planar, the Si–H bond length is 1.462 Å, and the fundamental stretching band is at 838.0674 cm^{-1}.

The gas-phase chemistry of silylium ions is versatile and includes unusual rearrangements, which differ substantially from the rearrangements of carbenium ions. The rearrangements of silylium ions require activation,[53, 54] whereas the rearrangements of carbenium ions can occur at very low temperatures and even in the solid phase.[55, 56]

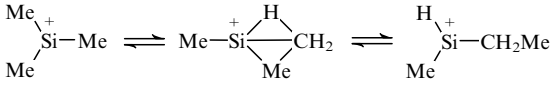
The mechanism of rearrangements of silylium ions differs from that of rearrangements of carbenium ions proceeding under the same conditions.[57–59] For example, dissociation of the *tert*-butyl cation in a mass-spectrometer chamber occurs primarily with elimination of methane[59]

$$[Me_3C]^+ \longrightarrow [CH_2{=}\overset{+}{C}{-}Me] + CH_4,$$

whereas dissociation of the trimethylsilyl cation results in elimination of an ethylene molecule[57–59]

$$[Me_3Si]^+ \longrightarrow [MeH_2Si]^+ + C_2H_4.$$

The mechanism of the latter rearrangement has been extensively studied over many years. Bakhtiar *et al*.,[57] who were the first to observe this rearrangement, described a mechanism involving isomerisation of the activated trimethylsilylium ion to give $EtMeHSi^+$ followed by elimination of ethylene. However, more recently it has been demonstrated[58] that these ions can undergo interconversions before elimination of ethylene.



Consequently, a less stable isomeric form of the silylium ion can be transformed into a more stable form if the activation energy is sufficiently high and the isomerisation barrier is lower than the dissociation threshold. Analogous isomerisation of the $C_2H_7Si^+$ ion was also studied:[53, 57–60]

$$Me_2HSi^+ \rightleftharpoons EtH_2Si^+.$$

Since the Me_2HSi^+ ion is more stable than the EtH_2Si^+ ion by 22.5 kcal mol^{-1},[53] the amount of the Me_2HSi^+ ions increases with increasing kinetic energy of the EtH_2Si^+ ions[60] (Fig. 1). At

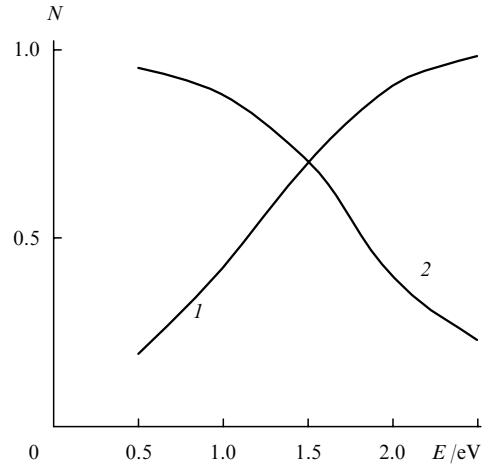


Figure 1. Yields of the Me_2HSi^+ (*1*) and EtH_2Si^+ (*2*) ions *vs*. the activation energy.[58]

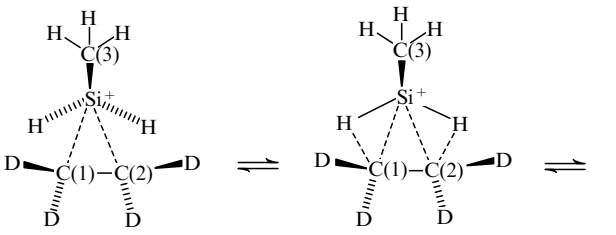
higher energies, dissociation of the EtH_2Si^+ ion with elimination of ethylene occurs.

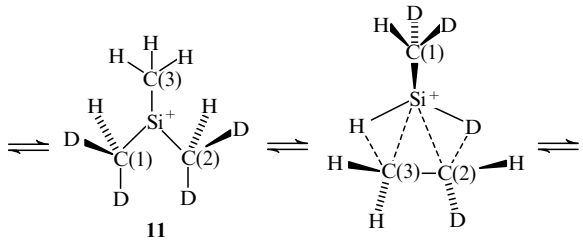
According to the results of mass-spectrometric studies,[57,58] 90% of the EtH_2Si^+ ions are isomerised into the thermodynamically more stable Me_2HSi^+ ions. Evidently, in this case the isomerisation barrier is lower than the energy required for elimination of ethylene. A totally different situation is observed for the $EtMeHSi^+$ ion. The isomerisation and dissociation barriers of this ion have similar heights,[54] due to which its isomerisation to the trimethylsilylium ion proceeds by only 5%.[61]

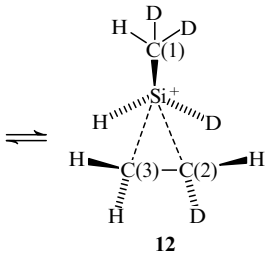
Only 28% of the $C_2H_7Si^+$ ions decompose to form ethylene.[62] Dissociation of $C_2H_7Si^+$ affords hydrogen molecules as the major product (72%). It appeared that the composition and the kinetic energy of the reaction products are independent of the isomer type of this ion, *viz*., Me_2HSi^+ or EtH_2Si^+. This suggests that the equilibrium between the isomers is established prior to dissociation. By contrast, the isomers of the $C_3H_9Si^+$ ion, *viz*., Me_3Si^+ and $EtMeHSi^+$, decompose to give primarily ethylene (89% and 97%, respectively) and differ substantially in the kinetic energy.

Structural isomers of silylium ions, unlike those of carbenium ions, can be distinguished by qualitative reactions.[60,61] Isomerisation of the ethylsilylium ion to the dimethylsilylium ion was confirmed by the isotope exchange between this ion and perdeuterated ethylene. In the disubstituted R_2HSi^+ ion (R = Me or Et), only the silicon-bound ^1H atom can be exchanged for deuterium, whereas all hydrogen atoms in the monoalkyl-substituted RH_2Si^+ ion can be involved in the isotope exchange.[60]

The theoretical explanation of this phenomenon was given in the study.[53] The proposed mechanism of the reaction of MeH_2Si^+ with C_2D_4 involves the formation of the $[MeH_2Si^+ \cdot C_2D_4]$ complex (**10**) as an intermediate followed by the migration of the hydrogen atoms from the silicon atom to the ethylene moiety to give the asymmetrical $Me(CD_2H)_2Si^+$ cation (**11**) *via* a transition state **TS1** with a minimum energy.







The reverse transformation of ion **11** into the starting complex can involve the unlabelled methyl group. In this case, complex **12** is, for example, formed *via* a transition state **TS2**. Its subsequent dissociation affords the $(CD_2H)HDSi^+$ ion and the $H_2C=CDH$ molecule. The perdeuterated methylsilylium ion can be obtained by repeating these processes many times. The reaction of Me_2HSi^+ with $CD_2=CD_2$ produces the $Me_2(CD_2CD_2H)Si^+$ ion as the most stable isomer. Its transformation can afford only Me_2DSi^+ and $HDC=CD_2$, *i.e*., only the hydrogen atom bound to silicon can be replaced by the deuterium atom. The hydrogen exchange between the methyl and silyl groups does not occur due to a high energy barrier.

Wojtyniak and Stone[63] made a substantial contribution to investigations of the reactivity of silylium ions with respect to nucleophilic reagents. They studied the gas-phase reactions of the Me_3Si^+ ion with alcohols, ethers, esters and aromatic hydrocarbons at a pressure of 3–5 mm Hg and a temperature from 298 to 600 K by mass spectrometry. The reactions gave the $[Me_3Si^+ \cdot B]$ adducts (B = AlkOH, AlkOAlk′, $AlkCO_2Alk'$ or ArH). The equilibrium constants of the reactions of the Me_3Si^+ cation with the oxygen-containing bases B_1 and B_2

$$[Me_3Si^+ \cdot B_1] + B_2 \rightleftharpoons [Me_3Si^+ \cdot B_2] + B_1$$

were measured and the relative basicities of these compounds towards Me_3Si^+ were determined from these constants. The change in the free energy of this reaction served as a measure of the basicity.

The basicity of various alcohols and water was demonstrated to increase in the same order as the proton affinity: butanol > propanol > ethanol > methanol > water.

It should be noted that the energy of association of alcohols with the Me_3Si^+ ion is higher than that with the Me_3C^+ and Me_3Sn^+ ions by ~20 and 7 kcal mol^{-1}, respectively (Table 1). For all cations, the energy of association increases with increasing basicity of alcohol ROH, *i.e*., with increasing length of the alkyl substituent.

Table 1. Changes in the enthalpy ΔH_0 (kcal mol^{-1}) of the reaction $[Me_3E^+ \cdot B] \rightarrow [Me_3E]^+ + B$.[63]

B	E		
	C	Si	Sn
H_2O	11.7	30.1	25.7
MeOH	22.8	39.2	32.6
EtOH	26.9	42.0	34.8
Pr^iOH	24.9	43.9	–

The difference in the energies of association of the Me_3Si^+ and Me_3C^+ ions with alcohols can be attributed to a higher positive charge density on the silicon atom compared to that on the carbon atom due primarily to the different degree of interaction between the unoccupied orbital of these cations and the orbitals of the methyl substituents.[64] For example, analysis of the populations of the unoccupied p_z orbitals demonstrated[65] that the population in the H_3Si^+ and H_3C^+ ions is virtually equal to zero (the orbital is actually unoccupied), whereas the population in the Me_2HC^+ and Me_2HSi^+ ions increases to 0.37 and 0.1, respectively. The electron density transfer to the carbon atom is much more substantial than that to the silicon atom. The inductive effect of the methyl substituents in the Me_3C^+ ion also leads to certain delocalisation of the positive charge on the cationic centre. In the Me_3Si^+ cation, the positive charge delocalisation due to the presence of the alkyl substituents is virtually absent because the electronegativity of silicon is lower than that of carbon.

The higher energy of association of the Me_3Si^+ ion with alcohols compared to that of the Me_3Sn^+ ions is apparently attributed to the larger volume of the tin atom and, consequently, the larger Sn–O bond length in the adduct.

The energy of association of the above-considered Me_3E^+ ions (E = C, Si and Sn) changes in the same order as that observed for other oxygen-containing compounds (for example, for ethers and esters).[63] Consequently, due to the larger positive charge

density on the silicon atom compared to that on the carbon atom and the smaller volume of silicon compared to tin, the trimethylsilylium ion is the most reactive species in this series with respect to oxygen-containing compounds in spite of the fact that the position of silicon in the Periodic table is between a typical non-metal (C) and a metal (Sn).

The basicity of different classes of oxygen-containing compounds towards the Me_3Si^+ cation changes in the following series: water < alcohols < ethers < esters.[63]

The energies of association of the Me_3Si^+ and Me_3Sn^+ ions with aromatic hydrocarbons (ArH), such as mesitylene and *o*-xylene, have similar values, which are slightly smaller than the energies of association with oxygen-containing compounds. Below are given the changes in the enthalpy (kcal mol^{-1}) of the reactions

$$[Me_3E^+ \cdot ArH] \longrightarrow [Me_3E]^+ + ArH.$$

E	ArH		Ref.
	mesitylene	*o*-xylene	
Si	31.1	29.2	63
Sn	32.0	29.9	66

A decrease in the difference between the energies of association of the Me_3Si^+ and Me_3Sn^+ ions with aromatic hydrocarbons can be explained in terms of hard and soft acids and bases.[67] For example, less polarisable silicon in the Me_3Si^+ ion more readily reacts with hard oxygen-containing bases, whereas the reaction of the Me_3Sn^+ ion becomes more preferable in the case of soft aromatic bases.

Amines are stronger bases than oxygen-containing compounds towards the trimethylsilylium ion. This is evident from the fact that the energies of association of the Me_3Si^+ ion with amines are substantially higher than those with alcohols. Table 2 gives the affinities (*i.e.*, the energies of association) of various amines to the Me_3Si^+ ion and the proton. As can be seen from Table 2, the affinity of amines to the Me_3Si^+ ion increases in the same order as the proton affinity: $NH_3 < MeNH_2 < EtNH_2 < Bu^nNH_2$, and it is determined by the increase in polarisability of the alkyl substituent in the amine.

Table 2. Affinities of amines to the Me_3Si^+ ion and the proton (kcal mol^{-1}).

Amine	Me_3Si^+ (see [68])	H^+ (see [69])
NH_3	46.5	204
$MeNH_2$	55.4	214.1
$EtNH_2$	57.4	217.0
Bu^nNH_2	59.5	218.4
Bu^sNH_2	57.9	220.5
Bu^tNH_2	58.0	220.8
Me_2NH	60.0	220.6

The basicities towards the Me_3Si^+ ion and the proton affinities of selected aromatic oxygen- and nitrogen-containing compounds were determined (Table 3).[70] As can be seen from Table 3, the characteristics of these compounds can be arranged in different series of increasing values because they are determined by different factors. For example, the basicities of compounds towards Me_3Si^+ can be influenced by steric factors, which have no effect on the proton affinity.[63] Nevertheless, these two characteristics equally depend on the nature of the substituents in the aromatic ring. In addition, as in the case of protonated organic compounds, the bonds between the Me_3Si^+ ions and the O (or N) atoms in adducts are essentially covalent in character.

Table 3. Relative basicities of aromatic compounds towards the Me_3Si^+ ion and the proton affinities (kcal mol^{-1}).

Compound	Me_3Si^+	H^+
PhC(O)H	36.2	191.7
PhC(O)Me	37.8	198.2
$PhNH_2$	35.5	203.3
$PhNMe_2$	39.5	217.3
Py	47.1	214.7

Therefore, the above-described studies showed that silylium ions not only are readily generated in the gas phase but also exhibit substantially higher affinity to π- and n-electron-donating compounds than carbenium ions.

2. Silylium ions in the condensed phase

The proof of the existence of silylium ions in the condensed phase is still a challenging problem of organosilicon chemistry. As we demonstrated above, conventional methods, which are generally used in organic chemistry for the generation of carbenium ions, are unsuitable for the synthesis of silicon analogues. Evidently, non-conventional approaches are required for the generation of silylium ions and investigation of their chemical behaviour in the condensed phase.

Studies by Lambert and co-workers (see, for example, Ref. 71) have opened a new stage in solving the problem of the synthesis of silylium ions in the condensed phase. Lambert proposed that silylium ions should be generated with the use of

— substituents at the silicon atom that enhance thermodynamic stability of silylium ions;

— counterions and solvents of low nucleophilicity;

— substituents creating steric hindrance to the approach of nucleophiles to the silicon centre.

All subsequent studies on the generation of silylium ions in the condensed phase were carried out taking into account these ideas.

In the chemistry of carbenium ions, the positive charge on the cation is stabilised primarily through π–π and n–π resonance interactions (for example, in the benzyl $PhCH_2^+$, allyl $CH_2=CHCH_2^+$ and methoxymethyl $MeOCH_2^+$ cations) and σ–π resonance interactions (in the *tert*-butyl cation Me_3C^+). By contrast, the electron-withdrawing inductive effect of such substituents as Ph, $CH=CH_2$ or OMe destabilises the carbenium ion. Consequently, the positive charge can be stabilised only if the π–π and n–π interactions not only compensate but are stronger than the undesired inductive effect, which is observed in the chemistry of carbenium ions. In the case of the silicon atom, resonance interactions with electronegative elements (N, O or F) are very weak and cannot compete with the destabilising inductive effect of the latter, due to which these elements are inefficient for stabilisation of silylium ions.

According to Lambert and Sun,[71] the positive charge in silylium ions can be stabilised by organosilicon substituents directly bound to the cation centre [for example, in the $Me_3SiMe_2Si^+$ or $(Me_3Si)_3Si^+$ ions]. Since the silicon atom is less electronegative and more polarisable than the carbon atom, the inductive effect of a silicon-containing substituent will stabilise the cation centre.

Quantum-chemical calculations demonstrated [72] that silylium ions can be efficiently stabilised by resonance 3p–3p interactions in the $(RX)_3Si^+$ or $(R_2X)_3Si^+$ cations, where X are third-period elements (X = S or P). Actually, the bond between the sulfur and silicon atoms is rather highly polarisable. In addition, the sulfur atom has 3p lone pairs and its electronegativity is approximately equal to that of the carbon atom (~2.5). For this reason, its inductive effect is expected to be smaller than that in the case of phenyl or oxygen-containing substituents.

Taking into account the above facts, the silylium ion $(Pr^iS)_3Si^+$ was prepared [73] by the Corey reaction. The hydride ion abstraction was performed with the use of triphenylmethyl perchlorate in dichloromethane or sulfolane. The conductivity of the resulting tris(isopropylthio)silyl perchlorate in both solvents

was as high as that of the starting triphenylmethyl perchlorate, which was attributed to the ionic character of the resulting salt.

However, other researchers have cast doubt on the validity of these results.[74, 75] For example, Olah and co-workers [74] attributed the conductivity of solutions of silyl perchlorates not to the ionic character of the products but to the formation of perchloric acid (due to the presence of traces of moisture) or complexation with solvent (Solv) molecules to give $[R_3Si-Solv]^+$. These complexes were described in the literature.[76, 77] It should be noted that information on the chemical shifts of silicon atoms in ^{29}Si NMR spectra of silylium ions, which could confirm or reject the results of investigations, was lacking in early 1980s.

The experimental chemical shifts of silicon atoms in perchlorates were generally observed at $\delta = 30-50$. The chemical shifts of the Me_3Si^+ and Ph_3Si^+ cations were predicted [78] ($\sim$250 and 125 ppm, respectively) based on the correlation with the carbon analogues. This is evidence that the free silylium ion was absent in the conducting perchlorates, and the latter existed as ionic complexes with the solvent, $[R_3Si-Solv]^+ClO_4^-$. More recently, quantum-chemical calculations confirmed this conclusion. For example, calculations by the IGLO (Individual Gauge for Localized Orbitals) method [79] gave the chemical shift of δ 355.7 for the silicon atom in the ^{29}Si NMR spectrum of the Me_3Si^+ ions, and the calculations by the GIAO (Gauge-Including Atomic Orbitals) method taking into account the electron correlation gave δ 385.[80] Later,[81] calculations with the use of the same methods gave δ 354 and 382, respectively.

Complexes of silylium ions with such solvents as pyridine, acetonitrile and imidazole were synthesised and their structures were estabished by X-ray diffraction.[82, 83] In all these structures, the bond between the silicon atom and the solvent molecule is only slightly longer than the typical covalent bond. According to Pauling, this is indicative of a small contribution of the ionic component. Calculations based on the crystallographic data showed [20] that the covalence of the silicon–solvent bond is 0.71 and the covalence of the Si–O bond in triphenylsilyl perchlorate is 0.68.

These studies led to the conclusion that a high degree of covalence of the bond between the silicon atom and halogen(or oxygen)-containing ions, as well as of the bond between the silicon atom and the solvent, in the complexes is a result of very high affinity of silicon to electronegative atoms. The ClO_4^- anion, which is generally used for stabilisation of organic cations, is a weak nucleophile, but its oxygen atoms very readily form bonds with silicon atoms. Such a solvent as sulfolane (tetrahydrothiophene 1,1-dioxide) has analogous properties. Consequently, the ability of the R_3Si^+ ion to form different types of complexes with nucleophiles, including the anion and solvent, forced researchers to look for alternative non-traditional conditions for the preparation of silylium ions.

It was found [84] that the Corey reaction can proceed in aromatic hydrocarbons, which have rather high polarisability and are not so strong nucleophiles as oxygen- and halogen-containing solvents. For example, the stannylium ions R_3Sn^+ were prepared with the use of aromatic solvents.[85]

An extensive search for anions for stabilisation of silylium ions performed in the last decades has demonstrated that non-nucleophilic anions do not exist at all. All anions with the lowest nucleophilicity (for example, perchlorate, triflate, hexachloroantimonate and tetrafluoroborate) contain halogen or oxygen atoms, which can easily be coordinated to the silicon atom. Attempts to use tetrafluoroborate BF_4^- (see Ref. 73) and tetraphenylborate BPh_4^- (see Ref. 86) as counterions for silylium cations also failed.

Publications on the preparation of positively charged zirconium ions by the Zr–C bond cleavage in tetrasubstituted organozirconium compounds under the action of tris(pentafluorophenyl)borane $(C_6F_5)_3B$ (see Ref. 87) and triphenylmethyl tetrakis(pentafluorophenyl)borate $[Ph_3C]^+[B(C_6F_5)_4]^-$ (see Ref. 88) provided evidence that these anions can be used as counterions for silylium ions. Actually, the fluorine atoms exhibit the negative inductive effect and withdraw the electron density from the benzene ring, thus decreasing the nucleophilicity of the latter. At the same time, a resonance interaction between the lone pairs of the fluorine atom with the aromatic ring leads to a decrease in the nucleophilicity of the fluorine atom. The combination of these two effects is responsible for low nucleophilicity of the $[B(C_6F_5)_4]^-$ anion.

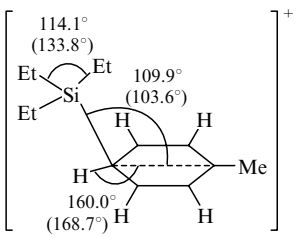
However, first attempts [84] to use this approach for the preparation of silylium ions failed due apparently to the fact that the C–Si bond in silyl hydrides is stronger than the C–Zr bond. Hence, various procedures were combined with the aim of preparing silylium ions. The latter were generated by the Corey reactions involving the cleavage of the weaker Si–H bond with the use of $[B(C_6F_5)_4]^-$ as the counterion and aromatic hydrocarbons (benzene or toluene) as the solvent. In some cases, this combined approach has led to success.[84, 89] It should be noted that free tricoordinate tris(2,4,6-triisopropylphenyl)stannylium ions were detected with the use of triphenylmethyl tetrakis(pentafluorophenyl)borate as well.[90, 91]

However, the experimental chemical shifts of silicon atoms in the ^{29}Si NMR spectra of the resulting silylium ions differ from the calculated values. For example, the chemical shift calculated [81] for the Et_3Si^+ ion by the GIAO and SOS–DFPT (Sum-Over-States Density Functional Perturbation Theory) methods is $\delta = 371.2$ and 415.6, respectively, whereas the experimental value is 92.3 ppm.[89]

The observed dependence of the ^{29}Si NMR signal on the nature of the solvent is direct evidence that the solvent is coordinated to the silylium ion. Based on these result, it was concluded that silylium ions did appear in aromatic hydrocarbons but as species weakly coordinated by solvent molecules rather than in the free state.[89]

In 1993, Lambert *et al.*[92] isolated crystals of triethylsilyl tetrakis(pentafluorophenyl)borate from toluene and established their structure. In this compound, coordination of the cation to the anion is completely absent; instead, the cation is weakly coordinated to the carbon atom of the solvent in the *para* position with respect to the methyl group. The $Si-C(sp^2)$ bond length was found to be 2.19 Å, *i.e.*, approximately 0.3 Å larger than the standard Si–C σ-bond length. In addition, the geometry of the toluene molecule is completely undistorted, which is indicative of a weak interaction with the silyl cation. Based on these data, Lambert [92] stated that he obtained the virtually 'free' silylium ion, which forms a π complex with the solvent molecule.

The above-described data have stimulated vigorous debates. The results of theoretical calculations [75, 93, 94] for the structure of the compound synthesised by Lambert suggested that a σ complex rather than a π complex was prepared. It was hypothesised that the $Si-C(sp^2)$ bond in this complex is covalent, the positive charge being to a large extent shifted from the silicon atom to the aromatic ring. The parameters of the $[Et_3SiC_6H_5Me\text{-}p]^+$ cation (**13**) determined by X-ray diffraction (in parentheses) and quantum-chemical calculations are given below.

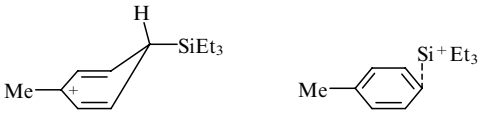


13

In this discussion, the main argument against the formation of the 'free' silylium ion is that the experimental chemical shift of the silicon atom observed in the ^{29}Si NMR spectrum of this compound ($\delta = 83.6$ in benzene [84]) differs substantially from the chemical shifts calculated for Me_3Si^+ [355.7 ppm (Ref. 75) and

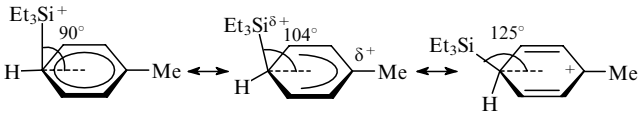
355 ppm (Ref. 79)] and Et_3Si^+ [371.2 ppm (Ref. 81)], whereas it is similar to the chemical shift calculated for the $[Me_3SiC_6H_6]^+$ complex [80.9 ppm (Ref. 75)]. In traditional organic chemistry, the structures of carbenium ions are, as a rule, beyond doubt due to a good agreement between ^{13}C NMR spectroscopic data and the results of quantum-chemical calculations.

Another important question was whether the compound synthesised by Lambert is σ complex **13a** or π complex **13b**.



13a **13b**

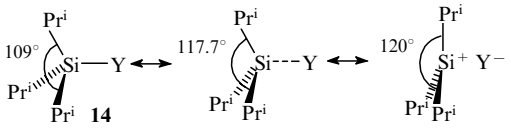
It was hypothesised[95] that the $[Et_3Si \cdot PhMe]^+$ cation is neither a pure σ complex nor a pure π complex but is a particular hybrid. The argument was that the $Et_3Si-C-C(para)$ angle in the complex synthesised by Lambert (104°) is intermediate between the values of this angle in the ideal π complex (90°) and the ideal σ complex (125°).



π Complex (**13b**) Observed complex σ Complex (**13a**)

In 1995, Reed and co-workers[96] synthesised crystalline trialkylsilyl(hexachloro)carboranes containing the silyl group structurally similar to the silyl cation. Halocarborane $(CB_{11}H_6Cl_6)^-$ was used as the anion of low nucleophilicity. In all the complexes under study, the cation and the anion were coordinated through the halogen atom involved in the anion. However, the distance between the silicon and chlorine atoms was rather large (2.23 Å).

The structure most similar to that of the silylium ion was observed in the $Pr^i_3Si(CB_{11}H_6Cl_6)$ (**14**), where the average angle $C(Pr^i)-Si-C(Pr^i)$ is 117.7°.



Y = $CB_{11}H_6Cl_6$.

Si–Y bond type:	covalent	ionic-like	ionic

The angle, the rather large $Si-Cl(CB_{11}H_6Cl_6)$ bond length (2.23 Å) and the fact that the $Si-C(Pr^i)$ bond length remains unchanged (1.85 Å) led the authors to conclude that the charges in this compound are sufficiently separated, which is an indication of the formation of silylium ions. Unlike the carbon chemistry, where the covalent compounds R_3CX are clearly distinguished from the carbenium ions $R_3C^+X^-$, trialkyl-substituted derivatives of silicon R_3SiX have a geometry characteristic of bonds intermediate between covalent (sp^3-hybridisation) and ionic (sp^2-hybridisation).

According to calculations[96] of the total energy for the model compound $Me_3Si^{\delta+}Cl^{\delta-}$, the degree of ionicity of compound **14** with the $C(Pr^i)-Si-C(Pr^i)$ angle of 117.7° is 60%.

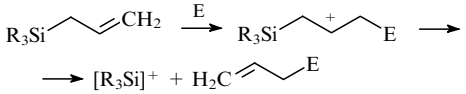
However, the chemical shift of the silicon atom in the ^{29}Si NMR spectrum of compound **14** (δ = 115) differs substantially from that calculated for the $Pr^i_3Si^+$ cation [δ = 342.3 (calculations by the GIAO method) and 371.0 (calculations by the SOS–DFPT method)[79]].

High-level calculations performed in 1996 (see Ref. 97) demonstrated that silylium ions can form complexes with weak Lewis bases, such as ethylene, benzene, bromomethane and fluoromethane, and even with methane and noble gases. This fact suggests that in none of the solvents the silylium ion can be isolated in the 'free state'. Hence, the problem is not to generate silylium ions but to estimate the degree to which the silylium ion in a complex with a solvent is cationic.

However, the final conclusion drawn by theorists has stimulated the research teams headed by Lambert and Reed to examine the possibility of introducing other substituents at the silicon atom with the aim of solving the problem of silylium ions. These substituents should not only stabilise the positive charge on the silicon atom but also cause steric hindrance to the approach of the anion or solvent molecules to the cation centre, thus preventing complexation. Since the *tert*-butyl and hexyl groups[21,89] are unsuitable for this purpose, 1,3,5-trimethylphenyl (mesityl, Mes) was chosen as the substituent. In this case, the charge can be stabilised by a resonance interaction between the silicon and the aromatic ring with the simultaneous protection of the cationic centre by steric hindrance due to the presence of the *ortho*-methyl substituents.

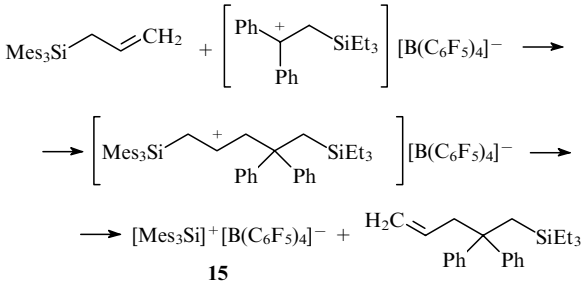
However, bulky substituents, in turn, make it impossible to generate silylium ions by the Corey reaction based on bimolecular‡ hydride ion abstraction from R_3SiH because such substituents hinder the approach of the carbocation to the hydrogen atom of the Si–H bond. Because of this, the hydride ion was replaced with the bulkier allyl (All) group (the chemical behaviour of All with respect to nucleophiles is similar to that of H).

As a results, the following reaction scheme was proposed for the synthesis of silylium ions:[98]



R = Mes, E is an electrophile.

In this case, the allyl group interacts with an electrophile, thus facilitating release of the silylium ion containing bulky substituents. Lambert *et al.*[98] applied this approach to the synthesis of the $[Mes_3Si^+][B(C_6F_5)_4]^-$ salt (**15**).



15

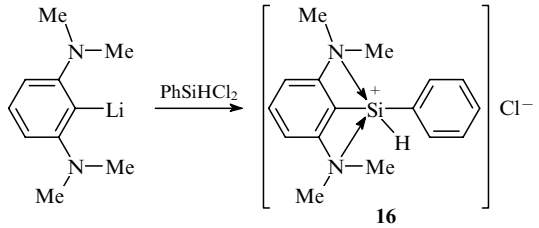
The chemical shift of the silicon atom (δ = 225.5) in the ^{29}Si NMR spectrum of compound **15** is similar to the calculated chemical shift for the Ph_3Si^+ cation (δ = 208.9). This suggests that at least the major portion of the positive charge is localised on the silicon atom. However, the question whether the silylium ion is 'free' can ultimately be answered only by demonstrating that the position of this signal is independent of the nature of both the solvent and anion. It was found that the silicon atom has similar chemical shifts in the ^{29}Si NMR spectra of trimesitylsilyl tetrakis(pentafluorophenyl)borate (**15**) in aromatic hydrocarbons: δ 225.5 in benzene, 225.7 in a 1 : 3 benzene–toluene mixture and 225.6 in a 1 : 1 benzene–*p*-xylene mixture. However, in acetonitrile this signal in the spectrum was observed at δ 37.0. Apparently, the acetonitrile molecule is so small that it can reach the cationic centre even in the presence of three bulky substituents at the silicon atom.

‡ Unlike carbenium ions, which are readily generated by the S_N1 mechanism, silylium ions can be generated only in bimolecular reactions due to high affinity of silicon to the leaving group.

After the replacement of the $[B(C_6F_5)_4]^-$ anion with the carborane derivative $(CB_{11}H_6Cl_6)^-$, the chemical shift in the ^{29}Si NMR spectrum remains virtually unchanged (225.9 ppm), which confirms the absence of complexation of the Mes_3Si^+ cation with these anions.[99] The calculated ^{29}Si chemical shift for the trimesitylsilylium ion in the equilibrium geometry is 230.1 ppm,[100,101] which is in good agreement with the experimental value (225 ppm).

Therefore, in spite of tremendous difficulties associated with the choice of the anion, the leaving group, substituents at the silicon atom and the solvent, the research teams headed by Lambert and Reed succeeded in demonstrating the possibility of the existence of the free silylium ion in the condensed phase.

The use of substituents containing electronegative heteroatoms with lone pairs (N or O) is yet another interesting way of stabilising the positive charge on the silicon atom. In this case, the so-called intramolecular stabilisation of the cationic centre can occur. Corriu and co-workers[102] was the first to synthesise this type of nitrogen-containing cations.

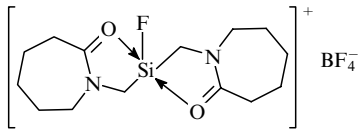


16

The ^{29}Si NMR spectrum of compound **16** confirms the structure of the pentacoordinate ion both in solution and in the solid state.

In the $[R_2SiC_6H_3(CH_2NMe_2)\text{-}2,6]^+$ cations (R = H or Me), the intramolecular coordination of silicon by the nitrogen atom is so strong that it prevents solvation with solvent molecules.[103]

Baukov and co-workers[104–106] synthesised silylium ions **17**, in which the positive charge is stabilised by the coordination interaction O→Si.



17

However, in spite of the fact that the positive charge on the silicon atom in these cations is stabilised, such structures can hardly be considered as classical free trivalent silylium ions.

A non-traditional radiochemical approach to solving the problem of the generation of silylium ions in the condensed phase was developed by a research group from St Petersburg.[17,107–111] This approach is based on the use of β-decay of tritium (incorporated in substituted silanes), which is independent of external conditions.

$$R_{4-n}SiT_n \xrightarrow{\beta^-} [R_{4-n}SiT_{n-1}]^+ + {}^3He$$

18

R = Me, Et, Ph; n = 1–3.

The uniqueness of this nuclear-chemical method is that it allows one to generate free (without a counterion and an equilibrium solvent shell) silylium ions with a desired charge localisation both in the gas phase in a wide pressure range and in the condensed phase. This method was used for the generation of the silylium ions Me_2TSi^+, EtT_2Si^+, Et_2TSi^+ and PhT_2Si^+, and the properties of these ions were studied (for details see Section IV.2).

3. Silylium ions as short-lived reaction intermediates

In spite of all difficulties associated with the generation of stable silylium ions in the condensed phase, their formation as short-lived intermediates was not ruled out; moreover, their formation in many reactions was postulated by analogy with carbenium ions. Comprehensive kinetic studies of the reaction mechanisms of organosilicon compounds are presently underway. Charged silylium species are assumed to be involved in these reactions. The hydride ion abstraction from the R_3SiH molecule with the use of carbenium ion resulting in the generation of the silylium ion R_3Si^+ (the above-considered Corey reaction) is one of such reactions.

Chojnowski *et al.*[112,113] studied the kinetics of this reaction in detail for silanes R_3SiH (R = Et, Bu, Ph, *etc.*) and the salts $[Ph_3C]^+BF_4^-$ and $[Ph_3C]^+SbF_6^-$. Investigation of the influence of the steric and electronic effects of the substituents at the Si atom on the reaction rate and the use of isotopic indicators led the authors to conclude that the electron transfer is the rate-determining step of the reaction. The second (fast) step gives silylium ions.

$$R^1_3SiH + [R^2_3C]^+X^- \xrightarrow{\text{step 1}} [R^1_3SiH^{+\bullet}X^- // R^2_3C^{\bullet}] \xrightarrow{\text{step 2}} [R^1_3Si]^+X^- + R^2_3CH$$

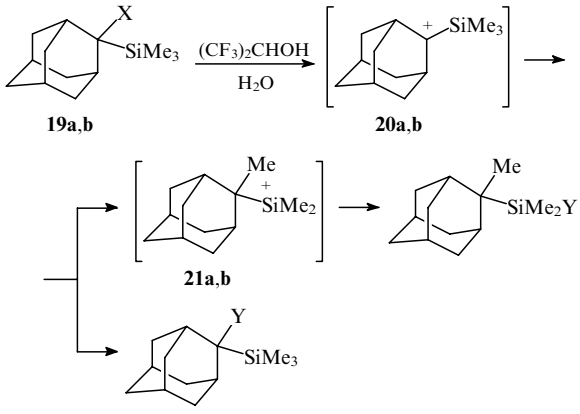
However, according to calculations,[114] the reaction mechanism involving electron transfer is energetically unfavourable, and the synchronous barrierless hydride transfer is the rate-determining step.

$$R^1_3SiH + [R^2_3C]^+X^- \longrightarrow [R^1_3Si]^+X^- + R^2_3CH$$

Studies on the influence of the steric and electronic effects of the substituents at the silicon atom on the reaction pathway of R_3SiH with the diarylcarbenium ions Ar_2CH^+ (Ar = Ph, *p*-Tol, *p*-$MeOC_6H_4$ and *p*-$PhOC_6H_4$) and investigation of the reaction mechanism demonstrated[115] that the formation of silylium ions is the rate-determining step of the process.

In the study of dimethyl(trimethylelementomethyl)silanes $(Me_3ECH_2)Me_2SiH$ (E = C, Si, Ge or Sn),[116] it was demonstrated that the steric and electronic effects, as well as the conjugation effects, which can stabilise the positive charge on the silicon atom, substantially influence the rate of reactions of these compounds with carbenium ions. This fact suggests that silylium ions are formed as reaction intermediates.

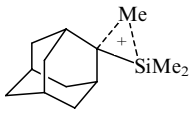
The formation of solvolysis products of 2-chloro- or 2-benzoyloxy-2-(trimethylsilyl)adamantanes (**19a**,**b**) in aqueous hexafluoropropan-2-ol was accounted for by the rearrangement of the initially formed carbenium ions **20a**,**b** into silylium ions **21a**,**b** through the 1,2-methyl shift.[117]



19a,**b** **20a**,**b** **21a**,**b**

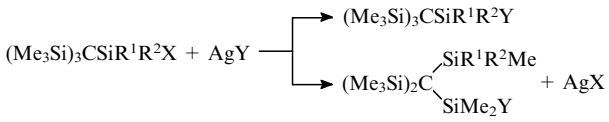
X = Cl (**a**), $O_2CC_6H_4NO_2$-4 (**b**); Y = OH, $OCH(CF_3)_2$.

The possibility of this rearrangement was confirmed by gas-phase studies and calculations, which provided evidence that silylium ions are thermodynamically more stable than carbenium ions. Alternatively, this reaction can be explained by the involvement of a non-classical bridged cationic intermediate **22** in this process.



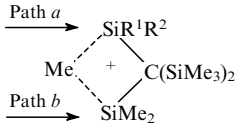
22

Eaborn [118] reasoned that bridged silylium ions of type **22** are formed as intermediate species in some reactions of organosilicon compounds containing bulky substituents, for example, $(Me_3Si)_3C$. In particular, Eaborn and co-workers demonstrated [119] that the reactions of compounds of the type $(Me_3Si)_3CSiR^1R^2X$ and $(Me_3Si)_2C(SiMe_2X)(SiR^1R^2X)$ with some electrophiles, including silver salts AgY (Y = AcO, CF_3CO_2, ClO_4, *etc.*), CF_3CO_2H and ICl_3, afford mixtures of rearranged and non-rearranged Si–X-bond cleavage products.



R^1, R^2 = Me, Et, Ph, *etc.*; X = Hal, H, *etc.*

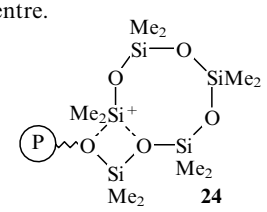
These results can most adequately be explained by the formation of a non-classical bridged ion **23**. In this process, the attack of the nucleophile on one end (path *a*) affords non-rearranged products, whereas the attack on another end (path *b*) gives rise to rearranged products.



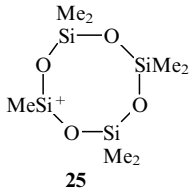
23

Dihalosilylenes SiX_2 (X = F, Cl, Br or I) generated in the gas phase and concentrated in a toluene solution in the presence of I_2 or ICl at −90 °C give mixtures of *ortho, meta* and *para* isomers of $MeC_6H_4SiX_2I$.[120] The authors attributed the formation of these compounds to the electrophilic attack of the short-lived cations X_2ISi^+ on the aromatic ring. The isomer ratio for X = Cl in the presence of I_2 was *ortho : para : meta* = 10 : 4 : 3, *i.e.*, the *ortho*-substituted isomer was the major product. When ethylbenzene was used as the solvent, the yield of the *ortho* isomer sharply decreased and the isomer ratio was 4 : 2 : 3. These results are attributed to the influence of the steric effects of the alkyl group and are consistent with the data obtained by Lambert.[92]

It was hypothesised [121, 122] that silylium ions are intermediates of radiation-induced polymerisation of permethylcyclosiloxanes $(Me_2SiO)_n$, where n = 3–5. The initial ionisation of the molecule occurs as a result of elimination of the methyl anion from cyclosiloxane. The authors postulated that the resulting silylium ions contain either a coordinated (**24**) or non-coordinated (**25**) cationic centre.



24



25

(P) is polymer.

The above-considered published data are conclusive proof of the formation of silylium ions postulated earlier as short-lived intermediates in organosilicon reactions.

IV. Ion-molecular reactions of silylium ions

1. Reactivity

The concepts 'reactivity' and 'thermodynamic stability' are closely related to each other. To estimate the reactivity of silylium ions, it is necessary to consider the factors responsible for stability of these ions.

The physicochemical properties of silicon suggest that silylium ions are thermodynamically more stable than isostructural carbenium ions. This is associated with both lower electronegativity of the silicon atom and its larger radius compared to those of the carbon atom (1.8 and 2.5,[123] 1.17 and 0.77 Å,[124] respectively). The ionisation potentials of the alkyl and silyl radicals, the enthalpies of formation of the silylium and carbenium ions and their hydride ion affinities are also indicative of higher thermodynamic stability of silylium ions compared to carbenium ions (Table 4).

Quantum-chemical calculations showed that the silylium cation H_3Si^+ is at least 54 kcal mol^{-1} more stable than the methyl cation H_3C^+.[131] However, this difference becomes substantially smaller in the presence of alkyl substituents, as well as π- and n-electron-donating substituents, in the cationic centre.[50, 132]

The relative stabilities of silylium ions can be estimated from the enthalpies of isodesmic § reactions (2)–(4).[50]

$$[R_nH_{3-n}Si]^+ + SiH_4 \longrightarrow R_nSiH_{4-n} + [H_3Si]^+ , \quad (2)$$

$$[R_nH_{3-n}C]^+ + CH_4 \longrightarrow R_nCH_{4-n} + [H_3C]^+ , \quad (3)$$

$$[R_nH_{3-n}Si]^+ + R_nCH_{4-n} \longrightarrow R_nSiH_{4-n} + [R_nH_{3-n}C]^+ , \quad (4)$$

n = 0–3.

The stabilisation energies of the $R_nH_{3-n}Si^+$ and $R_nH_{3-n}C^+$ ions calculated for these reactions are given in Table 5.

All the above-considered substituents, except for F, stabilise silylium ions. However, the stabilisation effect is substantially

§ Isodesmic reactions are reactions that involve only charge transfer, whereas the chemical bond configuration remains unchanged.[133]

Table 4. Thermodynamic characteristics of carbenium and silylium ions.

Parameter	Species	E = C		E = Si	
		value	ref.	value	ref.
Ionisation potential of radicals /eV	$H_3E^{\bullet}$	9.84	125	8.01	126
	$Me_3E^{\bullet}$	6.34	125	5.93	126
Hydride ion affinity /kcal mol^{-1}	MeH_2E^+	270.5	127	245.9	127
	Me_2HE^+	251.5	127	230.1	127
	Me_3E^+	233.6	127	220.5	127
Enthalpy of formation of the ion (ΔH°_{298}) /kcal mol^{-1}	H_3E^+	261.3	128	235.2	129
	MeH_2E^+	216.0	130	204.1	129
	Me_2HE^+	192.0	130	173.2	129
	Me_3E^+	166.0	130	145.0	129

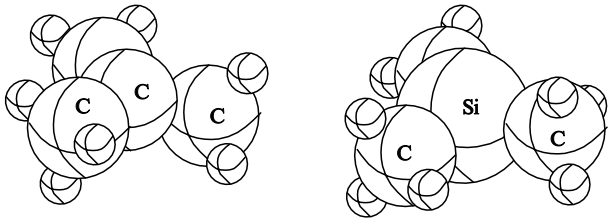
Table 5. Stabilisation energies of substituted silylium ($R_nH_{3-n}Si^+$) and carbenium ($R_nH_{3-n}C^+$) ions calculated[50] by the MP2(fc)/6-31G*// MP2(fc)/6-31G* method from the enthalpies of isodesmic reactions (2)–(4).

R_n	Stabilisation energy /kcal mol^{-1}		
	reaction (2)	reaction (3)	reaction (4)
H	0.0	0.0	57.4
Me	15.1	40.6	31.8
Me_2	27.9	58.7	26.6
Me_3	38.4	74.8	21.0
Ph	31.5	76.2	–
H_2N[a]	37.5	100.5	−5.6
$(H_2N)_3$	63.5	135.0	−22.8
HO	19.1	66.3	10.1
F	−1.1	25.3	31.0
H_3Si	12.3	16.5	53.2
$(H_3Si)_2$	20.0	–	–
$(H_3Si)_3$	24.9	–	–
H_2P	17.6	63.4	11.6
HS	18.5	63.6	12.2
Cl	2.2	29.2	30.3

[a] The results of calculations for the planar structure are given.

smaller than that in the case of carbenium ions. Silylium ions in the gas phase are always more stable than the corresponding carbenium ions. An increase in the number of substituents at the cationic centre stabilises silylium ions to a lesser extent than carbenium ions (see Table 5).

Substituents that cause steric hindrance to the approach of a nucleophile to the cationic centre, thus increasing stability of the latter, stabilise silylium ions to a lesser degree than carbenium ions. This is explained by a substantially larger atomic radius of silicon compared to that of carbon. The stereo projections of the Me_3C^+ and Me_3Si^+ ions calculated by the MP2(fc)/6-31G* method[50] are given below.



Therefore, in spite of the fact that the introduction of substituents of different nature and an increase in their number diminish the difference between stabilities of carbenium and silylium ions, the latter remain thermodynamically more stable.

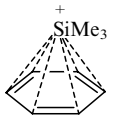
The high positive enthalpies of formation (ΔH°) (and, correspondingly, high free energies ΔG°) are indicative of the high reactivity of silylium ions, because the reactions can follow several pathways resulting in a decrease in the free energy of the system. Reactions of silylium ions are fast due to the presence of the unoccupied 3p orbital in these ions and the positive charge on the silicon atom. This leads to the appearance of a long-range polarisation interaction whose energy can be even higher than the activation energies of various transformations of a complex formed from the ion. The above-mentioned thermodynamic and kinetic requirements for ion-molecular interactions are equally characteristic of silylium and carbenium ions. However, as mentioned above, silylium ions are highly prone to expansion of the coordination sphere. As a result, these ions become even more electrophilic and can react with any nucleophile, including counterions and solvent molecules. That is why silylium ions, which are thermodynamically more stable in the gas phase than carbenium ions, remain virtually undetectable in the condensed phase.

Because of the difficulties in generating silylium ions in the condensed phase, their chemical behaviour in solution have remained unknown for many years. In the first studies dealing with this problem, ion-molecular reactions of the Et_2HSi^+ ions with benzene, dibutyl ether and (*tert*-butylamino)trimethylsilane were investigated by a radiochemical method.[108–111]

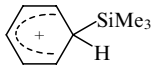
2. Ion-molecular reactions of silylium ions with π- and n-electron-donor compounds

Among chemical transformations of silylium ions, ionic silylation of nucleophilic reagents in the condensed phase is of particular interest.

Benzene is a classical representative of π-electron-donor compounds. The importance of electrophilic ionic alkylation of benzene in organic chemistry is difficult to overestimate. A different situation arises with electrophilic ionic silylation of aromatic compounds. First attempts to perform electrophilic silylation of benzene[63, 134] in the gas phase led only to the identification of an adduct to which the structure of π complex **26a** was assigned.



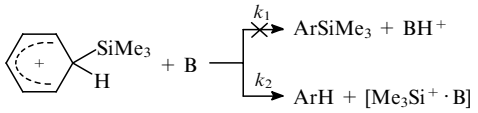
26a



26b

More recently, experimental[135–138] and theoretical[75] studies demonstrated that the reactions of silylium ions with aromatic compounds yield σ complex **26b**. Actually, the energies of association of silylium ions with aromatic compounds are even higher than those with their carbenium analogues (Table 6), and the role of the σ complex in electrophilic alkylation is well known.

In spite of the fact that the formation of σ complexes in the reactions of the H_3Si^+ and Me_3Si^+ cations with benzene and toluene was proved, silylation products of these aromatic compounds were not detected.[136] This can be attributed to the fact that, under the experimental conditions used, desilylation of σ complexes occurs much faster than their deprotonation ($k_2 \gg k_1$).



B is a Lewis base.

More recently, it has been demonstrated[136–138] that electrophilic silylation of benzene and toluene in the gas phase occurs only in the presence of strong proton acceptors (for example, of amines). Oxygen-containing bases induce predominantly desilylation.

A comprehensive insight into reactions of these species with nucleophilic compounds under different conditions was obtained for the first time with the use of the nuclear-chemical method of generation of silylium ions and a radiochemical approach to investigation of their reactions.[17, 107–111, 139–146]

Ion-molecular reactions of the ethyl- (see Ref. 139) and diethylsilylium ions[108, 109] with benzene in the gas and condensed phases in the absence of additives were studied by the radiochemical method. In the case of tritium-labelled ions, silylation products were identified for both cations. However, the ethylsilylium cation gives not the expected silane $PhSiH_2Et$ but its isomer $PhSiHMe_2$ in very low yield (4%); this reaction affords labelled benzene as the major product (96%). These data agree well with the mass spectrometric data and results of quantum-chemical calculations for the $C_2H_7Si^+$ ion.[54, 57, 58]

In the case of diethylsilylium ion, the reactions afford predominantly silylation products (>95%), whereas the yield of labelled benzene is 2%–5% (Table. 7).

The reaction products contain both the starting (Et_2HSi) and rearranged (EtH_2Si and Me_2HSi) silyl groups. Ethyl(dimethyl)-

Table 6. Experimental [135–138] and calculated [75] energies of association (kcal mol^{-1}) of silylium ions and *tert*-butyl cations with benzene.

σ Complex	Calculations		Experiment
	method	value	
$[H_3SiC_6H_6]^+$	HF/3-21G(*)//3-21G(*)	−51.1	–
	HF/6-31G*//6-31G*	−47.1	
	MP2(fc)/6-31G*//MP2(fc)/6-31G*	−54.8	
$[Me_3SiC_6H_6]^+$	HF/3-21G(*)//3-21G(*)	−25.2	−23.9
	HF/6-31G*//6-31G*	−20.5	
	MP2(fc)/6-31G*//MP2(fc)/6-31G*	−31.1	
[*ipso*-$Me_3CC_6H_6]^+$	MP2(fc)/6-31G*//MP2(fc)/6-31G*	−14.9	−22
[*p*-$Me_3CC_6H_6]^+$	MP2(fc)/6-31G*//MP2(fc)/6-31G*	−21.1	–
[*p*-$MeC_6H_5SiMe_3]^+$	HF/3-21G(*)//3-21G(*)	−29.7	−28.4
	HF/6-31G*//6-31G*	−25.1	
	MP2(fc)/6-31G*//MP2(fc)/6-31G*	−34.2	
[*p*-$CD_3C_6D_5SiMe_3]^+$	–	–	−31.3
[*p*-$MeC_6H_5CMe_3]^+$	–	–	−29.1
[*p*-$CD_3C_6D_5CMe_3]^+$	–	–	−28.6

Table 7. Relative yields of labeled reaction products of EtT_2Si^+ and Et_2TSi^+ with benzene.

Cation	Products [a]	Yields [b] (%)	
		gas phase	liquid phase
EtT_2Si^+	$PhSiHMe_2$	4	–
	PhH	96	–
Et_2TSi^+	$PhSiHEt_2$	13	32
	$PhSiH_2Et$	31	40
	$PhSiHMe_2$	54	23
	PhH	2	5

[a] The products contains the tritium label; [b] in the calculations of the yields, volatile silanes and ethylene formed in insignificant amounts were ignored.

phenylsilane resulting from the reaction with the most stable tertiary silylium ion Me_2EtSi^+, was not detected.

Quantum-chemical calculations of the potential energy surface of the $C_4H_{11}Si^+$ cation by the B3LYP/6-31G** method demonstrated [109] that isomerisation of the diethylsilylium cation giving rise to the most stable ethyl(dimethyl)silylium ion has to overcome two activation barriers. One of these processes gives the intermediate complex $[EtH_2Si^+ \cdot C_2H_4]$, whereas another process leads to the rearrangement into the most stable isomeric form Me_2EtSi^+ (Fig. 2). The dissociation threshold of the initially formed $[EtH_2Si^+ \cdot C_2H_4]$ complex (63.2 kcal mol^{-1}) is 5.3 kcal mol^{-1} lower than the isomerisation barrier (68.5 kcal mol^{-1}), which provides dissociation of the complex to form ethylene and the ethylsilylium ion. Consequently, even having the required energy, the Et_2HSi^+ ion does not undergo isomerisation to form the most stable tertiary cation Me_2EtSi^+, which is confirmed by the absence of ethyl(dimethyl)phenylsilane among the reaction products.

In spite of the fact that the ratios of the silylation products of benzene with ethyl- and diethylsilylium ions are substantially different, there is no reason to assume that these reactions proceed by different mechanisms. This is evidenced by the similar energies of complexation of the ethyl- and diethylsilylium ions with benzene (−39.7 and −31.2 kcal mol^{-1}, respectively, calculated by the B3LYP/6-31G** method) and the structure of a model intermediate **27**.[147]

The Si−C(1)−C(4) angle in the complex **27** (∼105°) is similar to the corresponding angle in classical π complexes (90°).

The charge distribution in the complex **27** was calculated by the NBO (Natural Bond Orbital analysis) method.[147] It appeared that the major positive charge (+0.99) is localised on the silicon atom. The positive charge on the hydrogen atom in the *ipso*

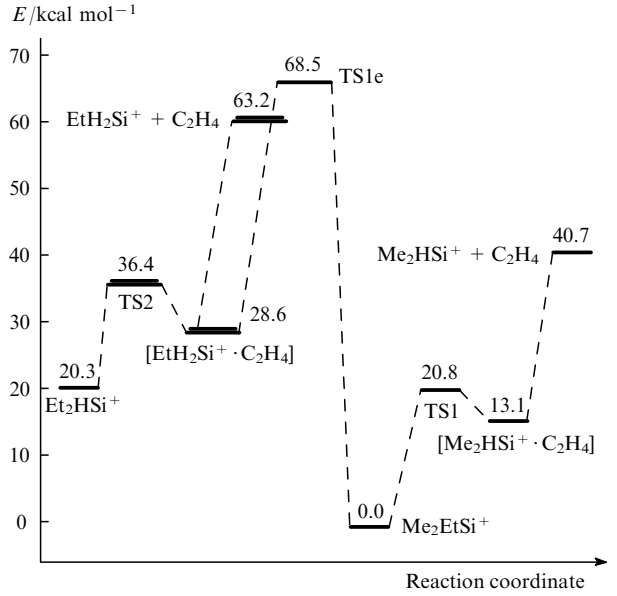
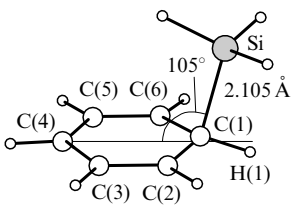
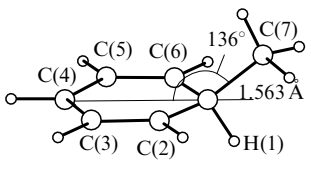


Figure 2. Potential energy surface for the transformations of the $C_4H_{11}Si^+$ cation.[109]

position (+0.33) is virtually equal to that on the other hydrogen atoms of the benzene ring (+0.28). Alkylation of aromatic compounds is known [148] to give covalently bonded σ complex **28** as an intermediate. In this complex, the angle between the alkyl group and the plane of the ring is ∼136°. The positive charge is transferred from the carbenoid carbon atom to the hydrogen atoms of the benzene ring, the charge being most substantially transferred to the *ipso* position (+0.36). The charge of the C(7) atom in the complex **28** is −0.65.



27



28

Evidently, the structure and the charge distribution in the σ complex formed by the reaction of silylium ions with benzene favour desilylation rather than deprotonation. The difference in

the experimental yields of the silylation products of benzene with ethyl- and diethylsilylium ions is associated with the difference in the ability of these species to be involved in the isotope exchange with the hydrogen atom in the *ipso* position. As a result, monomolecular decomposition of the σ complex with diethylsilylium ion affords tritium-free benzene as the major product.[108] The interconversions of the $C_2H_7Si^+$ and $C_4H_{11}Si^+$ ions proceed *via* ethylene complexes and can be accompanied by migration of silicon-bound tritium to the ethyl group.[109] Since only the silicon-bound tritium can be exchanged with the aromatic hydrogen atom, it is evident that the probability of this process in the case of diethylsilylium ions is substantially lower. Larger lability of the hydrogen atom in the monosubstituted ethylsilylium ion also leads to an increase in the rate of isotope exchange.

$$EtT_2Si^+ \rightleftharpoons [HT_2Si^+ \cdot C_2H_4] \rightleftharpoons (C_2H_4T)HTSi^+$$

$$Et_2TSi^+ \rightleftharpoons [EtTHSi^+ \cdot C_2H_4] \rightleftharpoons$$

$$\rightleftharpoons EtTHSi^+ + C_2H_4$$

$$\rightleftharpoons Et(C_2H_4T)HSi^+ \rightleftharpoons [EtH_2Si^+ \cdot C_2H_3T] \rightleftharpoons EtH_2Si^+ + C_2H_3T$$

Therefore, desilylation occurs as the major process in the case of both the Et_2HSi^+ and EtH_2Si^+ cations, as in the case of Me_3Si^+.[135–138]

High isomerisation barriers compared to the energy acquired by the silylium ion, which is generated by the nuclear-chemical method, upon the rearrangement of the tetrahedral structure into the planar structure [$\sim$22–24 kcal mol^{-1} (see Ref. 149)] suggest that isomerisation of silylium ions in the reaction with the benzene molecule occurs in an intermediate complex. The difference in the lifetime of the intermediate complex in the gas and condensed phases is responsible for the difference in the degree of isomerisation of the diethylsilylium ion. As a result, the percentage of products containing the rearranged silyl fragment is lower in the condensed phase.[108, 109]

The [$R_3Si^+ \cdot$ alkene] adduct [reaction product of alkenes with the R_3Si^+ ions (R = Me, Et)] and its subsequent transformations were studied [150] in the gas phase by the radiolytic method. A high concentration of the adduct is provided by a high pressure of a dilutant gas. It was found that this rather stable ionic adduct can decompose only in the presence of strong bases, *viz*., by deprotonation in the presence of amines (for example, Et_3N) or desilylation in the presence of oxygen-containing nucleophiles (for example, H_2O, MeOH, *etc*.).

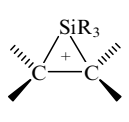
$$R_3Si^+ + \text{alkene} \rightleftharpoons [R_3Si^+ \cdot \text{alkene}] \longrightarrow$$

$$\xrightarrow{B} BH^+ + \text{silylation product}$$

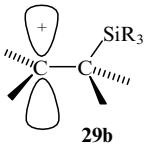
$$\xrightarrow{Nu} [R_3SiNu]^+ + \text{alkene}$$

The direct reaction of the ethylsilylium ion generated by the nuclear-chemical method with ethylene affords dimethylvinylsilane in low yield ($\sim$10%).[139]

The structures of the adducts of silylium ions with alkenes have been debated for many years. Both the bridged (**29a**) [151] and open (**29b**) [152] structures were considered.



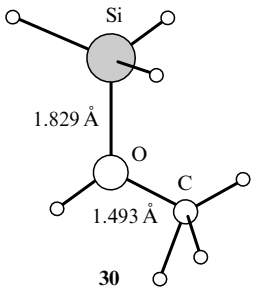
29a



29b

Quantum-chemical calculations demonstrated [109] that the resulting adduct is the bridged ethene complex, for example, [$EtH_2Si^+ \cdot C_2H_4$], located in a local minimum on the potential energy surface (see Fig. 2), which is 28.6 kcal mol^{-1} higher than the global minimum. Another local minimum, which is only 13 kcal mol^{-1} higher than the global minimum, corresponds to the ethene complex of the isomeric dimethylsilylium ion [$Me_2HSi^+ \cdot C_2H_4$]. A minimum corresponding to the open structure was not found.

Unlike π-electron-donor compounds, n-electron-donor compounds readily undergo silylation under the action of silylium ions. The reactions of the silylium ions $R_{3-n}T_nSi^+$ (R = Me or Et; n = 1 or 2) with alcohols [141–144] in the gas phase afford primarily silylation products, *viz*., the corresponding alkoxysilanes. These reactions give rather strong covalently bonded oxonium ions of type **30** (calculations by the B3LYP/6-31G** method for the adduct of H_3Si^+ and methanol) as intermediates. In the latter, the positive charge (+0.58, estimated by NBO) is localised to a large extent on the proton of the hydroxy group.



30

This proton is readily abstracted (for example, is transferred to substrate molecules), resulting in the formation of alkylalkoxysilanes from complexes of type **30**.

The oxonium complex can also undergo monomolecular decomposition with elimination of the carbenium or silylium ion to give the corresponding disiloxane or tritium-labelled alcohol.[141–144] The formation of the latter is attributed to isotope exchange between the hydrogen atom of the alcoholic hydroxy group and the tritium atom in the silylium ion. As with benzene, this exchange occurs much more easily in the case of the EtT_2Si^+ ion.[141–144]

The reaction of the diethylsilylium ions Et_2TSi^+ with yet another representative of n-electron-donor oxygen-containing compounds, *viz*., dibutyl ether, also proceeds *via* an oxonium complex **31**.[110] The exothermicity of the reaction is 72.7 kcal mol^{-1}.

$$[Et_2TSi]^+ + BuOBu \longrightarrow \left[\begin{array}{c} Bu-\overset{+}{O}-Bu \\ | \\ Et_2SiT \end{array}\right]$$

31

Taking into account the relaxation energy of the silylium ion,[149] the total excitation energy of the oxonium complex appears to be rather high, which facilitates its monomolecular decomposition with elimination of the diethylsilylium or the butyl cation.[110] Since there are no labile hydrogen atoms in this complex, its reactions with substrate molecules can lead only to energy transfer. Because of the absence of labile hydrogen atoms in the ether molecule, the isotope exchange, *i.e*., the formation of tritium-labelled dibutyl ether, becomes impossible. Consequently, the formation of silylation products ($Et_2TSiOBu$, EtT_2SiOBu and $Me_2TSiOBu$; the yield was 80%) in the gas and condensed phases is attributed to monomolecular dissociation of complex **31** with elimination of the butyl cation.[110]

The reaction of the Et_2TSi^+ ions with hexamethyldisiloxane gives an intermediate adduct **32** which decomposes according to the following scheme:

$$\left[\begin{array}{c} Me_3Si-\overset{+}{O}(-SiMe_3)-Et_2SiT \end{array}\right] \longrightarrow \underset{\mathbf{33}}{Me_3Si-O-SiTEt_2} + \underset{\mathbf{32}}{} \quad (5)$$

$$+ \underset{\mathbf{34}}{Me_3Si-O-SiMe_2CH_2T} + \text{other products}$$

Along with the main reaction product, *viz*., unsymmetrical disiloxane **33**, a series of disiloxanes containing rearranged terminal silyl substituents were identified.[145] Unlike the reaction with dibutyl ether, the reaction of the diethylsilylium ion with hexamethyldisiloxane affords, among other products, labelled substrate **34**. Hexamethyldisiloxane is an organosilicon ether. It contains no labile hydrogen atoms and, at first glance, would not form a labelled substrate. According to quantum-chemical calculations [the HF/4-21(O*)G method][153] for the model $H_3C^+ - Me_2O$ and $H_3C^+ - (H_3Si)_2O$ systems, the ether methyl group in the oxonium complex retains the tetrahedral structure, whereas the silyl group in the $[H_3C(H_3Si)_2O]^+$ complex is virtually planar. Apparently, the trimethylsilyl substituent in oxonium complex **32** is substantially ionic in character and can undergo isomerisation to give the EtMeHSi substituent containing the labile hydrogen atom. As a result, the isotope exchange between the hydrogen atom of the silyl fragment of the substrate and the tritium label in the diethylsilylium ion in the reaction (5) becomes possible.[145]

According to the results of mass spectrometry,[68] the reaction of the trimethylsilylium ion with n-butylamine gives the $[Me_3SiNH_2Bu]^+$ adduct as the major product, whereas the reaction of this cation with tributylamine involves two competitive processes. One process affords the $[Me_3SiNBu_3]^+$ adduct, whereas another process is accompanied by the hydride ion abstraction from the butyl substituent of the amine molecule under the action of the Me_3Si^+ ion to form the carbenium ion $[C_{12}H_{26}N]^+$. It should be noted that, in spite of the fact that the proton affinity of the Bu_3N molecule is higher than that of $Me_2Si=CH_2$, the reaction of the Me_3Si^+ ion with a mixture of Bu_3N and $BuNH_2$ gives the protonated tributylamine in insignificant amount. The authors hypothesised that this compound, unlike alkyl cations,[154–163] is formed in the reaction of the $[Me_3SiNBuH_2]^+$ adduct with tributylamine rather than due to the proton transfer from the trimethylsilylium ion to the tributylamine molecule.

$$[Me_3SiNBuH_2]^+ + Bu_3N \longrightarrow Me_3SiNHBu + [Bu_3NH]^+$$

The reactions of ethyl- and diethylsilylium ions with trimethyl(*tert*-butylamino)silane in the gas and condensed phases were studied by the radiochemical method.[111, 146]

It is known[154–163] that reactions of carbenium ions with organic and organosilicon amines follow two competitive pathways, *e.g*., occur as condensation (6) and proton transfer (7). In the former reaction, amine reacts as a nucleophile, whereas it acts as a base in the latter reaction. Silylium ions and amines are involved only in condensation (8), in spite of the fact that the proton transfer is not energetically forbidden.[111, 164]

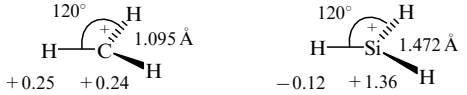
$$[T_3C]^+ + NH(SiMe_3)R \longrightarrow [T_3CNH(SiMe_3)R]^+ \quad (6)$$

$$[T_3C]^+ + NH(SiMe_3)R \longrightarrow [TNH(SiMe_3)R]^+ + :CT_2 \quad (7)$$

$$[Et_2TSi]^+ + NH(SiMe_3)R \longrightarrow [Et_2TSiNH(SiMe_3)R]^+ \quad (8)$$

R = Me_3C, Me_3Si.

This difference is associated with the difference in the electron density distribution in carbenium and silylium ions. According to quantum-chemical calculations,[147] the positive charge in the H_3Si^+ cations is virtually completely localised on the silicon atom, and the hydrogen atoms are hydride in character, whereas the positive charge in carbenium ions is uniformly distributed between the carbon atom and the hydrogen atoms.



In the condensed phase, the qualitative composition of the reaction mixture remains unchanged, and only the component ratio becomes different: the mixture contains a higher percentage of the products formed by bimolecular reactions whose efficiency increases in the condensed phase.[111]

Therefore, products containing the starting Et_2HSi group and the EtH_2Si and Me_2HSi groups as the silyl fragment were obtained in radiochemical studies of ion-molecular reactions of diethylsilylium ions with π- and n-electron-donor compounds (Table 8). Consequently, the rearrangement into ethyl- and dimethylsilylium ions takes place; this rearrangement is characteristic of diethylsilylium ions.[110, 111, 143–145]

$$[Et_2HSi]^+ \xrightarrow[-C_2H_4]{} [EtH_2Si]^+ + [Me_2HSi]^+$$

Table 8. The ratio of silylation products of oxygen-containing organic compounds and benzene with diethylsilylium ions.

Silyl substituent in the product	Ratio of silylation products (%) [a]			
	Bu_2O	BuOH	$(Me_3Si)_2O$	PhH
Et_2HSi	90	62	29	13
$EtH_2Si + Me_2HSi$	10	38	71	87

[a] The ratio was calculated from the relative yields of the corresponding silylation products.

The degree of this conversion is determined to a large extent by the nature of the electron-donor substrate. For example, for all studied oxygen-containing compounds and benzene, the percentage of products containing non-rearranged silyl substituents sharply decreases in benzene compared to that in dibutyl ether (see Table 8).[164] The activity series of the compounds inducing this rearrangement $Bu_2O < BuOH < (Me_3Si)_2O < PhH$ correlates with their nucleophilicities and is determined by the excitation energy of the intermediate complex and the possibilities of its transfer to the substrate molecules. The association energies calculated by a quantum-chemical method[164] for the H_3Si^+ ion and related model compounds increase in the following series (kcal mol^{-1}): PhH (47.6) < $(H_3Si)_2O$ (65.0) < MeOH (69.7) < Me_2O (72.7).

The minimum energy of association of the silylium ion with benzene ensures a longer lifetime of the complex and, as a consequence, the maximum degree of conversion. The opposite situation is observed for dibutyl ether. In this case, the degree of conversion is 10%, whereas the association energy of the similar model $H_3Si^+ - Me_2O$ system is the highest in this series of compounds (72.7 kcal mol^{-1}).

Although the calculated energies of association of the silylium ion with MeOH and Me_2O have similar values, the experimentally determined degree of conversion of the diethylsilylium ion in the reaction with butanol differs from that in the reaction with dibutyl ether. This is attributed to the different mechanisms of excitation energy transfer. In the case of alcohols, the complex undergoes both mono- and bimolecular decomposition, whereas only monomolecular decomposition can occur in the case of ethers.

From the above, it is clear that studies of ion–molecular reactions of silylium ions with nucleophilic reagents are in their infancy. The mechanisms of these transformations cannot be reliably established based on the results of mass-spectrometric

studies performed so far in the gas phase. The nuclear-chemical method of generation of silylium ions provides exhaustive information on their reactions with nucleophiles both in the gas and condensed phases. This method allows one to observe not only usual reaction products but also their isomeric forms, due to which more reliable conclusions about the mechanisms of reactions of silylium ions with nucleophilic compounds can be drawn.

* * *

Based on the above-considered data, the following conclusions can be drawn.

First, in spite of the fact that silylium ions have long been considered as analogues of carbenium ions, studies of the reactivity of the former ions have rejected this statement. The differences in the chemical behaviour are associated primarily with the difference in the electron density distribution in these cations. Second, the unique ability of the silicon atom to expand its coordination sphere results in higher electrophilicity of silylium ions compared to carbon analogues. Silylium ions can react with all types of nucleophiles, including counterions and solvent molecules, which make them undetectable in the condensed phase. Third, the existence of silylium ions as both reactive intermediates and individual species was unambiguously established with the use of non-traditional approaches to the generation of these ions in various media described in the present review. Nevertheless, it should be noted that further investigations of the properties of silylium ions will allow these species to play an important role in silicon chemistry.

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