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The Present State of the Problem of Silicenium Ions

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The present state of the problem of the existence and chemical behaviour of silicenium ions in the gas and condensed phases is examined and the principles of a new (nuclear-chemical) method for the generation of free silicenium ions, its characteristic features, and its advantages are described.
The bibliography includes 144 references.

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I. INTRODUCTION

The question of the possibility of the existence and the properties, reactivity, and role in the corresponding chemical processes of the silicon, germanium, and other analogues of carbenium ions is one of the most interesting in modern chemistry. The problem of the preparation and investigation of the properties of the silicon analogues of such ions is the most urgent at the present time.

Since silicon is less electronegative than carbon (their electronegativities are 1.8 and 2.6 respectively[1]), it was to be expected that silicenium ions would be formed at least as readily as carbenium ions and this is indeed the case in the gas phase.[1,2] The results of mass-spectrometric studies indicate the preferred formation, on energy grounds, of silicenium ions compared with carbenium ions.[2-4] However, many attempts to obtain silicenium ions in solution failed.[5-7]

Before proceeding to the consideration of various aspects of the problem of silicenium ions, it is essential to note that, apart from the great similarity in the chemical behaviour of silicon and carbon compounds, there exist also differences which can be accounted for in the first place by the presence of unoccupied *d* orbitals in silicon. The results of numerous investigations have shown that in its chemical behaviour silicon tends to expand its coordination (there is a transition from the sp^3 state to the sp^3d or sp^3d^2 state) and not to contract it, as happens in the case of carbon (transitions from the sp^3 state to the sp^2 and *sp* states).

It was believed for a long time that, in contrast to carbon, silicon is incapable of forming multiple $p_\pi-p_\pi$ bonds. However, since 1967 communications began to be published[8-10] in which the formation of unstable silicon compounds with Si=Si bonds was reported. In 1981-82 the first stable compounds with Si=C and Si=Si bonds were obtained.[11-13] In addition the $p_\pi-d_\pi$ bond, which is unknown for carbon, exists in silicon compounds.[14,15] It arises as a result of a shift of the π electrons in a neighbouring X atom (where X is a halogen, an aryl group, oxygen, nitrogen, etc.) to the unoccupied *d* orbitals of silicon. As a result of such $p_\pi-d_\pi$ bonding, the Si-X bond has a partial double bond character. The smaller length of the Si-X bond compared with the value calculated from the covalent radii, the widening of the valence angle in excess of the usual tetrahedral value, the reduction of the electron-donating capacity of the X atom on formation of a hydrogen bond, etc. are usually regarded as evidence for the $p_\pi-d_\pi$ interaction.[15]

Two aspects must be distinguished in the study of the problem of silicenium ions. The first concerns the possibility of the existence of silicenium ions in crystals and solutions as independent species. The second aspect involves the possibility of the appearance and existence of these ions as intermediate species. The problem of silicenium ions will in fact be considered below in terms of these two main features.

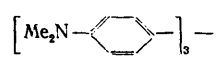
II. SILICENIUM IONS IN CONDENSED PHASES

1. Silicenium Ions as Independent Species in Solutions and Crystals

When attempts were made to demonstrate the existence of silicenium ions, organosilicon compounds which should have given rise to the corresponding ions under suitable conditions, by analogy with carbon compounds, were considered in the first place. Many investigators tried to show that the silicenium ion Ph_3Si^+, analogous to the stable ion Ph_3C^+, can exist. However, it has been demonstrated by a conductimetric method that there is no appreciable ionisation of Ph_3SiCl in pyridine, in a mixture of nitrobenzene with $AlBr_3$, or in liquid sulphur dioxide, although it is well known that all these solvents induce the ionisation of Ph_3CCl:[16]

$$Ph_3CCl \rightarrow Ph_3C^+ + Cl^-.$$

Another attempt consisted in the study of the properties of the silicon analogue of chlorotris(*p*-dimethylaminophenyl)-methane, which is an ionic compound. It was established by means of a number of methods (conductimetry, IR and UV spectroscopy, and X-ray diffraction) that

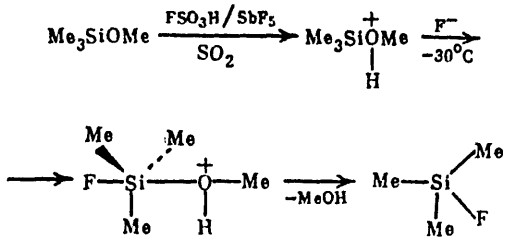


is a covalent compound.[17,18]

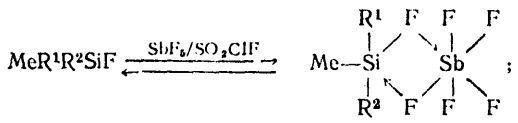
A number of studies were designed to compare and investigate the properties of silicon perchlorates.[19,20] It was demonstrated that the silicon perchlorates R_3SiClO_4 (where R = Me, Et, n-Pr, *p*-MeC_6H_4, or Ph) have a covalent structure, in contrast to the intensely coloured triarylmethyl perchlorates.

An attempt has been made[21,22] to obtain classical silicenium ions in the $FSO_3H/SbF_5/SO_2$ superacids whose nucleophilic properties are extremely weak. In this medium secondary and tertiary carbenium ions are stable and can be generated from organic compounds of different classes. The behaviour of alkoxysilanes and siloxanes in the above medium was studied at a low temperature by NMR and it was shown that

the oxygen atom is protonated, this being followed by a substitution reaction which leads to fluorosilane. R_3Si^+ ions were not detected. The formation of fluorosilanes can be accounted for by the appearance of a pentacovalent intermediate:

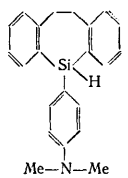


The behaviour of the fluorosilanes Me_3SiF in the SbF_5/SO_2. .ClF medium, in which stable carbenium ions can be detected, has also been studied.[23] However, in this case too the silicenium ions R_3Si^+ were not detected as independent species. The authors suggested that an involved complex having the following structure may be formed:[23]



$R^1 = R^2 = Me$; $R^1 = Me$, $R^2 = F$; $R^1 = R^2 = F$.

Corey and co-workers[24,25] reported the synthesis of silicenium ions from a compound which they synthesised, i.e.



by abstracting a hydride ion from the latter. However, later these results were disproved.[26,27]

The cause of the failure of the above investigations has apparently been the fact that the authors began with the hypothesis that there is a complete analogy between the properties of carbon and silicon, which is not always justified. For example, it is known that carbenium ions are readily stabilised as a result of the resonance $2p-2p$ transition between the carbenium atom and the ligand atoms linked to it. However, a simple interaction is much weaker in silicenium ions, where the silicon atom is linked to the elements of the Second Period (a resonance $2p-3p$ transition).[28] Calculations have shown that a more effective stabilisation can be achieved as a result of the resonance $3p-3p$ interaction in structures of the type $(RX)_3Si^+$ or $(R_2X)_3Si^+$, where X = S, P, or elements of the Third Period.[29,30] These ideas have been confirmed experimentally by Lambert and Schultz,[31] who attempted to obtain substituted silicenium ions by abstracting a hydride ion from tris(2-propylthio)silane in accordance with the mechanism

$$(iso\text{-}PrS)_3SiH + Ph_3C^+ClO_4^- \rightarrow Ph_3CH + (iso\text{-}PrS)_3Si^+ClO_4^-.$$

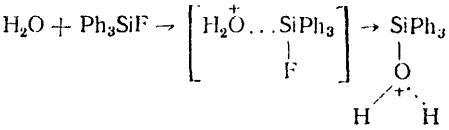
These investigations (conductrimetry, IR and UV spectroscopy, and NMR) led to results which agreed with the hypothesis of the formation of silicenium ions in this reaction.

The set of studies examined, including the last, indicate the lack of a final solution of the problem concerning the possibility of the existence of silicenium ions as independent species and the necessity for its further investigation.

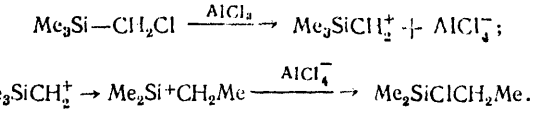
2. Silicenium Ions as Intermediate Species in Reactions of Organosilicon Compounds

Apart from the existence of silicenium ions as independent species, their involvement as intermediates in reactions has been frequently postulated. One of the first experiments designed to demonstrate the possibility of the formation of silicenium ions as reaction intermediates has been a kinetic study of the solvolysis of fluorotriphenylsilane.[32] The authors of this investigation observed a marked dependence of the rate of reaction on the nucleophilic properties of the medium. Thus Ph_3SiF reacts ten times faster in the presence of OH^- ions than in a neutral medium (acetone–water), while the rate of hydrolysis of Ph_3CF, which is the carbon analogue of the above compound, is independent of the pH of the medium. In addition, *p*-methyl substituents, introduced into fluorotriphenylsilane, decreased the rate of reaction by a factor of five, while their introduction into fluorotriphenylmethane increased the rate of reaction. This shows that a positive charge does not arise on the silicon atom in the transition state.

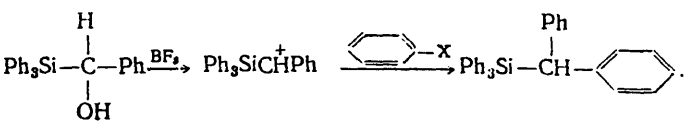
Bearing in mind the foregoing, Swain et al.[32] put forward a mechanism involving the formation of an intermediate pentacovalent silicon complex:



The rearrangement of organosilicon compounds with functional α-groups under the influence of Lewis acids is of interest from the standpoint of the possibility of the formation of silicenium ions as intermediates.[33–35] One of the proposed mechanisms is the Wagner–Meerwein mechanism:

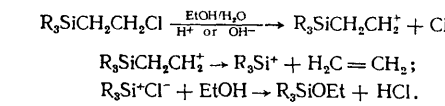


The formation of stable silicon-containing carbenium ions has indeed been demonstrated for these reactions both by direct observation and with the aid of the Friedel–Crafts reaction:[34]

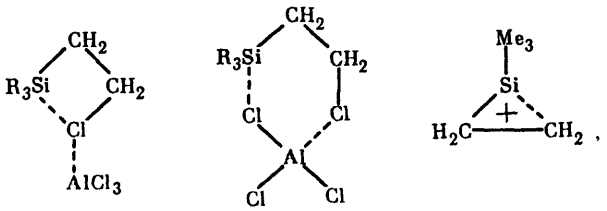


On the other hand, silicenium ions were never detected in these systems.

The hydrolysis of β-halogenoalkylsilanes has been investigated[36] and an ionic mechanism has been proposed for the reaction:



However, in this case too the formation of silicenium ions was not confirmed. The ionic mechanism has been criticised.[37,38] Other explanations of the formation of the observed products were based on the hypothesis that the reaction proceeds via a mechanism involving the appearance of complexes incorporating four-membered (A) or six-membered (B) rings[33] or via a stage in which a non-classical carbenium ion (C) is formed:[38]



(A) (B) (C)

The formation of the latter has been confirmed by the fact that the reactivity of compounds with functional β-groups is much higher than might have been expected as a consequence of the inductive effect of the Me_3SiCH_2 group.[39] This means that the C–X bond is cleaved under the influence of precisely the R_3Si group, in agreement with the structure of the non-classical carbenium ion.[38] Despite this, one cannot rule out the possibility that the above rearrangement proceeds via a mechanism involving the formation of silicenium ions, because such ions have been detected in a similar rearrangement in the gas phase.[40]

An ionic mechanism has also been proposed for the disproportionation of halogenosilanes under the influence of Lewis acids:[41–43]

$$R_2SiHCl + AlCl_3 \rightarrow [R_2SiH]^+ + [AlCl_4]^-;$$
$$R_2SiHCl + [R_2SiH]^+[AlCl_4]^- \rightarrow R_2SiH_2 + [R_2SiCl]^+[AlCl_4]^-;$$
$$[R_2SiCl]^+ + [AlCl_4]^- \rightarrow R_2SiCl_2 + AlCl_3.$$

However, no evidence in support of the proposed mechanism was obtained in this case either.

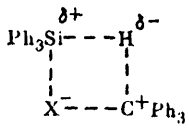
Reactions accompanied by racemisation are of special interest in the study of the possibility of the appearance of silicenium ions as intermediates. In the case of carbon compounds racemisation as a rule indicates the formation of a carbenium ion with the sp^2 structure as an intermediate form. However, the reactions are highly stereospecific for silicon compounds (>95%). Even in the presence of substituents such as aryl, vinyl, and allyl[44] a high stereospecificity was observed, indicating the absence of silicenium ions with the classical structure in the reactions of organosilicon compounds. In contrast to this, the analogous carbon compounds racemise very rapidly under solvolysis conditions as a result of the formation of the corresponding carbenium ions. However, one should note that in many cases optically active halogenosilanes do racemise.[45–54]

We shall consider the racemisation of halogenosilanes induced by certain solvents.[48,49] Conductrimetric measurements indicate the absence of any appreciable ionisation. The hypothesis of the formation of an ion pair has been put forward as an explanation, but it proved inconsistent with the absence of conductivity in the reaction medium. Further investigations showed that, among solvents capable of inducing the racemisation of chlorosilanes, there are some with a low dielectric constant, for example ethers ($\varepsilon < 15$), and also polar aprotic solvents.[54] The latter are especially interesting because they behave as effective ligands for elements with unoccupied *d* orbitals, since they form coordinate bonds readily. Analogous results have been obtained for optically active germanium compounds.[55,56] It has been suggested that the racemisation proceeds via a mechanism involving the formation of penta- and hexacoordinate intermediate silicon compounds. This hypothesis has been confirmed by the finding that bulky substituents at the silicon atoms retard the racemisation. The rate of racemisation involving the formation of the R_3Si^+ cation should have increased with increasing bulk of the substituents. This has been explained by the fact that, with increase of the bulk of substituents, their mutual repulsion should also increase, which facilitates the formation of the R_3Si^+ cation and hinders the formation of penta- and hexacoordinate intermediate compounds.

In order to demonstrate the possibility of the formation of silicenium ions as intermediate species, the hydride transfer reaction has also been investigated.[57–59] The ability of carbenium ions to act as acceptors of hydride ions was used for this purpose.[60] Formally, when a hydride ion is abstracted from silane by a carbenium ion, a silicenium ion, which is an analogue of the carbenium ion, should be formally produced:

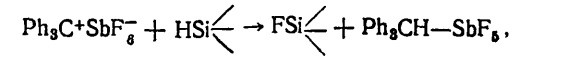
$$Ph_3C^+ + HSiR_3 \rightarrow Ph_3CH + R_3Si^+.$$

However, the appearance of silicenium ions has not been demonstrated for numerous silanes.[57–59,60] On this basis, a mechanism postulating the formation of a complex with a four-membered ring has been proposed for the hydride transfer reactions:[61]



Reactions of this type include the hydrogenation of olefins or the hydrogenolysis of alcohols by silanes in an acid medium.[62,63] Like those examined above, these reactions proceed via the formation of carbenium ions, which then abstract a hydride ion from the silane. However, the formation of silicenium ions in these reactions was also not demonstrated. The absence of silicenium ions as kinetically independent species can apparently be accounted for by the presence in the silicon atom of occupied *d* orbitals, which are responsible for the tendency of organosilicon compounds, including silanes,[64] to associate with nucleophiles with expansion of the outer electron shell.[1]

However, in a study of the kinetics of the hydride transfer from a silane to a carbenium ion in the reaction



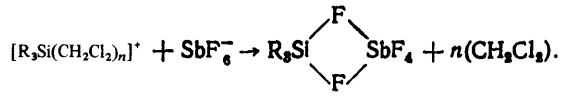
it has been observed[65] that the rate of appearance of the silane R_3SiH is higher than the rate of formation of the fluorosilane R_3SiF, which conflicts with the four-centre synchronous mechanism. In addition, it had been shown earlier that the stereochemical course of the reaction depends on the solvent.[58] This shows that the four-centre mechanism may not be the only one possible and does not rule out the possibility of the formation of an intermediate in which the positive charge is localised on the silicon atom.[66] It has been suggested[65] that the reaction proceeds with participation of silicenium ions and involves at least three stages.

The first stage is the hydride transfer leading to the formation of a positively charged silicon intermediate:

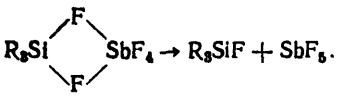
$$Ph_3C^+ + HSiR_3 \xrightarrow{n(CH_2Cl_2)} Ph_3CH + [R_3Si(CH_2Cl_2)_n]^+.$$

The second stage involves the formation of an uncharged

intermediate:

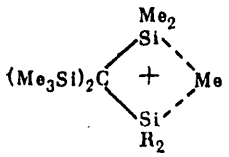


The third stage involves the decomposition of the uncharged intermediate with formation of the final products:



The reactions of organosilicon compounds containing the bulky tris(trimethylsilyl)methyl groups $(Me_3Si)_3C$ have been investigated.[67-70] The presence of these groups gives rise to steric hindrance in the nucleophilic attack on the silicon atom and hence makes it possible to observe reactions of an unusual type.

Thus, when the organosilicon iodides $(Me_3Si)_3CSiR_2I$ react with silver and mercury salts and also with halogens in methanol, the bridged silicenium cation (I)



(I)

is formed according to the authors.[67-70] The cation can also be attacked by nucleophiles, which is accompanied by the formation of rearrangement products of the type $(Me_3Si)_2C(SiR_2Me)(SiMe_2X)$.

A kinetic study of the solvolysis of the silicon perchlorate $(Me_3Si)_3CSiMe_2OClO_3$ has been carried out[71] in the presence of the salts NaOMe, LiCl, $LiNO_3$, and $NaClO_4$. The results of the kinetic investigations of the solvolysis were consistent with an S_N1 mechanism. It was suggested that the reaction also proceeds via the formation of the bridged silicenium cation (I).

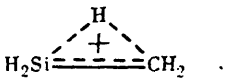
Thus the results of studies of the behaviour of organosilicon compounds in condensed phases are contradictory and, in contrast to carbon compounds, they can be partly interpreted without resorting to the idea that classical silicenium ions are formed as stable species or as reaction intermediates. This is apparently associated with the characteristics of the electronic structure of silicon distinguishing it from carbon (the presence of unoccupied *d* orbitals, the greater size of the silicon atom, its lower electronegativity, etc.) and its high nucleophilicity caused by these features.

III. SILICENIUM IONS IN THE GAS PHASE

1. Energy Relations in the Formation of Silicenium Ions

Whereas all attempts to demonstrate the existence of silicenium ions in the condensed phase have been unsuccessful, the formation of these species is a common phenomenon in rarefied gases, where they arise from organosilicon compounds under the influence of electron impact. Furthermore, the results of studies of the energetic conditions in the formation of tervalent silicenium ions have shown that their stability in the gas phase is greater than that of the analogous carbenium ions. Thus the heat of formation of the H_3Si^+ ion is 890 kJ mol^{-1}, while the heat of formation of the methyl cation H_3C^+ is 1090 kJ mol^{-1}.[72] The heat of formation of the H_3Si^+ ion has also been published[4] as 970 kJ mol^{-1}, which is somewhat greater than the value quoted in the above study[72] but is lower than the heat of formation of the methyl cation. The situation is analogous also as regards substituted silicenium ions. Thus the heat of formation of the trimethylsilicenium ion is 580 kJ mol^{-1},[1] 590 kJ mol^{-1},[3] or 610 kJ mol^{-1} [4] according to the data of different investigators; evidently all these data are in good agreement. On the other hand, the lowest of the known heats of formation of the trimethylcarbenium ion is 680 kJ mol^{-1},[73] i.e. is much higher than that of the trimethylsilicenium ion.

It has been shown[74] that the principal ion formed when methylsilane is bombarded by electrons having an energy of ~100 eV is the methylsilyl cation $MeSiH_2^+$. In the mass spectrum of deuteriated methylsilane $MeSiD_3$, the peak at *m/e* 47, corresponding to the $MeSiD_2^+$ ion, is 10 times higher than the peak at *m/e* 48, corresponding to the $D_3SiCH_2^+$ ion. In addition, non-empirical calculations have shown[75] that the heat of formation of the methylsilyl cation $MeSiH_2^+$ is higher by 190 kJ mol^{-1} than that of the silylmethyl cation $H_3SiCH_2^+$ and by 170 kJ mol^{-1} than that of the non-classical bridged ion



Thus the available theoretical and experimental data agree with one another.

The heats of formation of certain other tervalent silicenium ions have also been determined.[76,77] Thermodynamic calculations using the bond dissociation energies[76] as well as data for the vertical ionisation potentials of the radicals $RSiH_2^{\bullet}$ [76] and $RCH_2^{\bullet}$ [78] have shown that the silylcarbenium ions $H_3SiCH_2CH_2^+$ isomerise exothermically to the ethylsilicenium ions $EtSiH_2^+$ ($\Delta H = -120$ kJ mol^{-1}).[77]

Naturally the available information about the heats of formation of various silicenium ions is as yet insufficient, but analysis of the existing data already indicates that the energetic conditions in the formation of silicenium ions in the gas phase are more favourable than in the formation of the analogous carbenium ions.

2. Ion–Molecule Reactions of Silicenium Ions

In the general case ion–molecule reactions are understood as interactions of ions with neutral molecules accompanied by a change in either the elemental composition or in the charge or energy state of the species involved in such a process. Depending on the ratio of the time of the interaction (collision) between the ion and the molecule and the characteristic time of the transitions between the states of the colliding species, the mechanisms of ion–molecule reactions are divided into two types: direct reactions[79-86] and reactions proceeding via a mechanism involving the formation of a long-lived complex.[87,88]

Ion–molecule reactions proceed via the direct mechanism when the kinetic energy of the relative movement of the partners exceeds the energy of their polarisation attraction: $E_k > \alpha e^2/2r^4$ (here $\alpha e^2/2r^4$ is the energy of the polarisation interaction of the ion and the molecule over a distance *r*, equal to the sum of the radii of the ion and the molecule, and E_k is the kinetic energy of the relative movement of the ion and the molecule). The simplest model describing the direct mechanism is that of the direct stripping mechanism proposed by Henglein.[86] According to this model, the

transfer of energy from the species to the reactant ion takes place over a very short period. The possibility of the transfer of momentum to the residual species is then ruled out and its velocities before and after collision differ little. In such reactions, it is possible to predict the energy distribution of the products. Thus, when a hydride ion is transferred from the silane molecule to the reactant ion, the kinetic energy of the movement of the product ion is equal to the thermal energy (like the energy of the silane molecules) and the neutral product formed is characterised by the same kinetic energy as the reactant ion (i.e. a considerable energy).

The second type of ion–molecule reactions includes those involving the formation of a long-lived complex.[87,88] The reactions proceed via this mechanism when the energy of the polarisation interaction exceeds the kinetic energy of the relative movements of the ion and the molecule, i.e. subject to the condition $E_K < \alpha e^2/2r^4$; this condition is a criterion of the stability of the complex. The capture of the ion by the polarisation orbital of the molecule, which leads to the mutual approach of the colliding species to distances of the order of atomic dimensions, proceeds via this mechanism for certain parameters of the ion–molecule collision process. For such distances, the kinetic energy of the colliding species can be consumed in the excitation of internal degrees of freedom, which entails the formation of a long-lived complex whose decomposition yields the final products.[87,88]

Numerous mass-spectrometric studies of ion–molecule reactions of silicenium ions have been published recently. These include the investigations of ion–molecules reactions in pure silane,[89–91] in methylsilane,[92,93] in mixtures of silane with organic compounds,[77,94–100] the studies of ion–molecule reactions of carbenium ions with alkylsilanes,[101–103] the study of the intramolecular and intermolecular rearrangements of organosilicon compounds,[40,104–110] and also the study of the ion–molecule reactions of trimethylsilicenium ions with organic and organosilicon compounds.[111–114]

(a) Ion–molecule reactions in silane and its substituted derivatives. Studies of the reactions in methane, whose main products are the ions CH_5^+ [115] and $C_2H_5^+$,[116] are known to have played a major role in the development of our knowledge about ion–molecule reactions:

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + Me; \quad (1)$$

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2. \quad (2)$$

In the study of reactions occurring in silane, it is therefore of interest to compare the latter with processes characteristic of methane. Table 1 presents certain data for methane and silane which are of interest for the investigation of the gas-phase ion–molecule reactions of these compounds.

It is seen from Table 1 that, in contrast to methane, silane is not stable in relation to decomposition into its constituent elements. The ionisation of silane requires less energy than the ionisation of methane and much less energy must be expended on the formation of the SiH_2^+ and SiH_3^+ ions from silane than on the formation of the CH_2^+ and CH_3^+ ions from methane. The dipole moment of the Si–H bond has the opposite direction and should be much greater than the dipole moment of the C–H bond.

It has been shown[122] that the peak corresponding to the H_5Si^+ ion, which is analogous to the H_5C^+ ion in the case of methane, is absent from the mass spectra of monosilane (at pressures from 10^{-5} to 10^{-1} mmHg). Consequently a reaction analogous to reaction (1), in which the H_5Si^+ ion might have been formed, does not occur in the case of silane.[122] On the other hand, the absence of the SiH_4^+ ion can be readily accounted for with the aid of the data in Table 1. Using the ionisation potentials of the molecules and the appearance potentials of the ions (Table 1), it can be shown that the enthalpies of reactions (3) and (4) are only 60 and 20 kJ mol^{-1} respectively:

$$SiH_4^+ \rightarrow SiH_3^+ + H; \quad (3)$$

$$SiH_4^+ \rightarrow SiH_2^+ + H_2. \quad (4)$$

Table 1. Some properties of methane and silane.

Parameter	CH_4	SiH_4
ΔH_f^0, kJ mol^{-1}	−70 [117]	30 [117]
$D(H_3E-H)$, kJ mol^{-1}	430 [117]	350–400 [118]
$Ip(EH_4)$, kJ mol^{-1}	1220 [117]	1130 [119]
$Ap(EH_4^+/EH_4)$, kJ mol^{-1}	1380 [117]	1190 [118]
$Ap(EH_2^+/EH_4)$, kJ mol^{-1}	1470 [117]	1150 [118]
μ, D	+0.4 [121]	−1.6 [120]

Notation: ΔH_f^0 is the standard enthalpy of formation, $D(H_3E-H)$ the dissociation energy of the H_3E-H bond, Ip the ionisation potential, Ap the appearance potential, and μ the dipole moment.
Note. The numbers in square brackets denote references (Ed.of Translation).

The enthalpies of the corresponding processes involving methane are 150 and 240 kJ mol^{-1}. Hence it follows that the SiH_4^+ ion, formed from the silane molecule, cannot be stable, bearing in mind the Franck–Condon principle, relative to the SiH_3^+ and SiH_2^+ ion and its peak is therefore absent from the mass spectrum of silane.

The principal ion in the system considered is SiH_3^+,[89–91] which is the product and reactant ion simultaneously:

$$SiH^+ + SiH_4 \rightarrow SiH_2 + SiH_3^+;$$
$$SiH_2^+ + SiH_4 \rightarrow SiH_3 + SiH_3^+;$$
$$SiH_3^+ + SiH_4 \rightarrow SiH_4 + SiH_3^+.$$

It is noteworthy that the H_3Si^+ ion was believed for a long time to be insufficiently active,[90] since a sharp rise was observed along the initial section of the curve relating the intensities of the peaks of this ion in the mass spectrum to the pressure (Fig.1). This finding showed that the rate of reaction of the SiH_3^+ ion in the region of low pressures is much lower than the rate of its formation. However, further investigation of the behaviour of this ion demonstrated that it is extremely active.[91] The point is that the main reaction of this ion involves the transfer to the hydride ion from silane, which results in the appearance of the same silyl cation. In order to elucidate the mechanism of this hydride transfer, the kinetic energy of the product ion was analysed using the deuteriated silane SiD_4 as the substrate.[91] The results of the analysis showed that the hydride ion transfer reaction proceeds mainly via the direct stripping mechanism.

However, there are also processes proceeding via a mechanism involving the formation of a long-lived complex, which is indicated by the presence of isotopically mixed

products:[91]

$$SiH_3^+ + SiD_4 \rightarrow [Si_2H_3D_4]^+ \begin{cases} \rightarrow SiD_3^+ + SiH_3D; \\ \rightarrow SiD_2H^+ + SiH_2D_2; \\ \rightarrow SiDH_2^+ + SiHD_3; \\ \rightarrow SiH_3^+ + SiD_4. \end{cases}$$

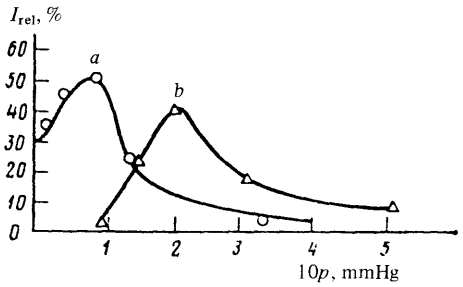


Figure 1. Dependence of the peak intensities of the SiH_3^+ (*a*) and $Si_2H_7^+$ (*b*) ions on pressure.[90]

Mass-spectrometric studies of the processes occurring in ionised methylsilane have been carried out in order to elucidate the role of the substituent (the methyl group).[92,93] One of the main ions (24%) formed on bombardment of methylsilane is $MeSiH_2^+$.[93] A characteristic reaction of this ion in methylsilane involves the abstraction of a hydride ion, as for unsubstituted silicenium ions. When the deuteriated methylsilane $MeSiD_3$ was used, it was shown that a hydride ion is abstracted from a Si–H bond and not from a C–H bond:[93]

$$MeSiH_2^+ + MeSiD_3 \rightarrow MeSiH_2D + MeSiD_2^+.$$

This is apparently due to the fact that the hydrogen in the Si–H bond is of the hydride type, while that in the C–H bond is of the proton type. The isotope distribution in the product ions shows that, as for silane, hydride transfer takes place mainly via the stripping mechanism; however, for low collision energies, processes involving the formation of a long-lived complex also take place.[93,123]

A mass-spectrometric study of $MeSiD_3$ showed that the hydrogen atoms in the methyl group are not involved in the hydrogen redistribution between the interacting species in the complex.[93]

Thus the C–H bonds are not involved in the hydride transfer reaction in silanes which proceed both via the direct mechanism and via the mechanism in which a long-lived complex is produced.

(*b*) *Ion–molecule reactions in silane–hydrocarbon mixtures.* Mass-spectrometric study of an ionised silane–hydrocarbon mixture is of great interest, because it becomes possible to follow simultaneously the ion–molecule reactions of silicenium and carbenium ions and to compare their chemical behaviour.

Processes in a silane–methane mixture have been investigated mass-spectrometrically in a number of studies.[94–96] The dominant processes in this system are the formation reactions of the H_3Si^+ ion via the mechanisms

$$CH_n^+ + SiH_4 \rightarrow CH_{n+1} + SiH_3^+, \text{ where } n = 0, 1, 2, 3; \quad (5)$$

$$CH_m^+ + SiH_4 \rightarrow CH_{m-1} + H_2 + SiH_3^+, \text{ where } m = 4, 5. \quad (6)$$

It has been shown[123] that the $C_2H_5^+$ ion, which is the main product of the ion–molecule reactions in methane, also reacts with silane to form exclusively the SiH_3^+ ion.

The possibility of the formation of the SiH_3^+ ion via proton transfer to the silane, postulated initially by some workers,[124] i.e.

$$CH_4^+ + SiH_4 \rightarrow [SiH_5^+]^* + CH_3 \rightarrow SiH_3^+ + H_2;$$
$$CH_5^+ + SiH_4 \rightarrow [SiH_5^+]^* + CH_4 \rightarrow SiH_3^+ + H_2.$$

is ruled out because the SiH_5^+ ion has not been detected even at a pressure of 0.5 mmHg.[96] If these processes did take place, one might have detected the SiH_5 ion stabilised by collisions at high pressure. The absence of the above proton transfer has been confirmed also by experiments carried out with fully deuteriated methane CD_4.[95] Within the limits of experimental error, the only silicenium ions in the mass spectrum are the SiH_3^+ ions.

We shall consider the reactions occurring in the silane–ethylene mixture. The main reactions in this case are also those involving the transfer of a hydride ion from silane to the attacking cation, which results in the formation of the SiH_3^+ ion:[7,97,125]

$$SiH_4 + C_2H_2^+ \rightarrow SiH_3^+ + C_2H_3;$$
$$SiH_4 + C_2H_3^+ \rightarrow SiH_3^+ + C_2H_4;$$
$$SiH_4 + C_2H_4^+ \rightarrow SiH_3^+ + Et.$$

In its turn, the silyl cation interacts with ethylene to form the complex $SiC_2H_7^+$, which is stabilised by collisions at high pressure. In the absence of stabilisation, this complex decomposes into the initial reactants or reaction products. Thus the interaction of the silyl cation with ethylene can be represented by means of the following schemes:

$$SiH_3^+ + C_2H_4 \rightarrow [SiC_2H_7^+]^* \rightarrow SiH_3^+ + C_2H_4;$$
$$[SiC_2H_7^+]^* \begin{cases} \rightarrow SiC_2H_5^+ + H_2; \\ \rightarrow SiCH_3^+ + CH_4; \\ \rightarrow SiC_2H_3^+ + 2H_2; \end{cases}$$
$$[SiC_2H_7^+]^* + C_2H_4 \rightarrow [SiC_2H_7^+] + C_2H_4^*.$$

A study[77] has shown that the majority of the collisions between the SiH_3^+ ion and the C_2H_4 molecule lead to the initial reactants. This can probably be accounted for by the fact that there exists a potential barrier separating the $H_3SiCH_2.CH_2^+$ ions formed initially from the more stable isomeric form $EtSiH_2^+$. The majority of the $H_3SiCH_2CH_2^+$ ions decompose rapidly into the reactants and only a small proportion isomerise to the $EtSiH_2^+$ ions. These ions and their dissociation products are in fact detected mass-spectrometrically. The maximum energy transmitted by the complex $EtSiH_2^+$ to the ethylene molecule on stabilisation by collision has been determined as 0.6–0.8 eV.[77] This is in good agreement with the results of a study[126] where it has been reported that the ethylene molecule is capable of accepting an excitation energy up to 1.3 eV without decomposition on collision within the excited species.

We shall now consider the ion–molecule reactions in the silane–benzene mixture.[99,100] The main product ions in this system as as follows; $C_6H_6^+$ (*m/e* 78), $SiC_6H_7^+$ (*m/e* 107), and $SiC_6H_9^+$ (*m/e* 109). It has been shown that the $SiC_6H_9^+$ ion is a long-lived complex with a lifespan of 10^{-5} s. At a high pressure this complex is stabilised by collisions, while in

the absence of stabilisation it decomposes into the reaction products $C_6H_6^+$ and $SiC_6H_7^+$. One can therefore put forward the following mechanism of the interaction of the silyl cation with benzene:

$$SiH_3^+ + C_6H_6 \rightarrow [SiC_6H_9^+]^*;$$

$$[SiC_6H_9^+]^* \begin{cases} \rightarrow C_6H_6^+ + SiH_3; \\ \rightarrow SiC_6H_7^+ + H_2; \end{cases}$$

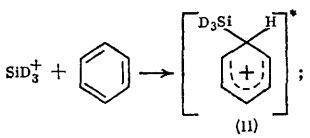
$$[SiC_6H_9^+]^* + C_6H_6 \rightarrow [SiC_6H_9^+] + C_6H_6^*.$$

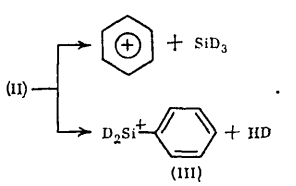
With increase of the kinetic energy of the reactant ion, the yield of the energy-enriched complex $SiC_6H_9^+$ falls sharply, while the relative yield of the product $SiC_6H_7^+$ falls much more slowly and the yield of the $C_6H_6^+$ ion increases sharply, reaching 70%. The unimolecular decomposition of the long-lived complex $[SiC_6H_9^+]^*$ also involves the formation of other ionic products in insignificant yields ($C_6H_7^+$, $SiC_4H_5^+$, and $SiC_4H_7^+$). Among these product ions, the $C_6H_7^+$ ion which is believed[100] to be formed on proton transfer from the silyl cation to benzene via the mechanism

$$SiH_3^+ + C_6H_6 \rightarrow C_6H_7^+ + SiH_2.$$

is of greatest interest. Analogous processes have been observed in the interaction of methyl cations with certain aromatic hydrocarbons, for example, with toluene.[127]

Experiments using fully deuteriated silane have shown[100] that the SiD_3^+ ion in the $SiC_6H_9^+$ complex retains its individuality and there is virtually no exchange of the hydrogen and deuterium ions in the complex. This permits the conclusion that the short-lived complex is an ion with a structure analogous to that of the σ-complex (II) and not an ion of the troplyium type. The interaction of the silyl cation SiD_3^+ with benzene can then be formulated schematically in the following manner:





The structure of the benzyl type (III) had already been proposed earlier in a study of the ionisation of phenylsilane by electron impact.[128]

The interaction of the methyl, ethyl, and butyl cations with methylsilanes having the general formula Me_nSiH_{4-n}, where n = 0, 1, 2, 3, or 4, has been reported.[101-103] The characteristic reactions of the above carbenium ions with methylsilanes are reactions involving hydride transfer from the silane to the attacking ion with formation of a tervalent silicenium ion $Me_nSi^+H_{3-n}$ and also processes involving the abstraction of the methyl anion from the silane and its transfer to the carbenium ion with formation of the $Me_{n-1}Si^+H_{4-n}$ ion.

The probabilities that the hydride ion or the methyl anion are split off are not the same for different carbenium ions.[103] The probabilities that the methyl and ethyl cations are split off are almost the same. In the case of the propyl cations the transfer of the methyl anion begins only in the presence of three methyl groups, while for the butyl cations four methyl groups are needed in the silane molecule.

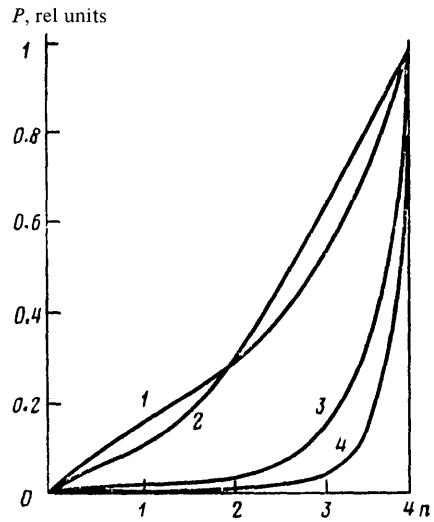


Figure 2. Dependence of the relative probability P of the transfer of the methyl anion on the number of methyl groups n in the methylsilane for different carbenium ions: *1*) CH_3^+; *2*) $C_2H_5^+$; *3*) $C_3H_7^+$; *4*) $C_4H_9^+$.[103]

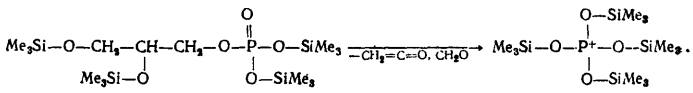
Fig. 2 illustrates the relative probabilities of the transfer of the CH_3^- ion from the silane Me_nSiH_{4-n} by various cations. The observed differences in the behaviour of the cations have been explained[103] by the fact that the propyl and butyl cations have the iso-structure. This hypothesis is consistent with the report[129] that the ionisation of neopentane by electron impact involves mainly the formation of the Me_3C^+ cation. Otherwise the propyl and butyl cations would have behaved in the same way as the ethyl cation.

The reactions of the methyl and ethyl cations with ethylsilanes of the type Et_nSiH_{4-n}, where n = 0, 1, 2, 3, or 4, were investigated and it was shown that the transfer of an alkyl anion is not observed in methylsilane systems only.[102,103]

The studies considered have shown that it is possible to obtain three silicenium ions in a rarefied gaseous phase from the corresponding silanes with the aid of electron impact and by the interaction of various carbenium ions with silanes.

(c) *The ion–molecule reactions of trimethylsilicenium ions.* The next stage in the study of silicenium ions involved the investigation of the reactions of trimethylsilicenium ions with organic and organosilicon compounds belonging to various classes. An important step in this research consisted of studies devoted to questions concerning the rearrangement of the silicenium ions themselves.[40,104-110] The majority of such rearrangements can be accounted for by the localisation of the positive charge on the silicon atom and by the subsequent formation of a bond between

silicon and the electronegative centre, usually the oxygen atom:[104–110]

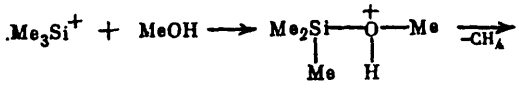


Apart from the peaks of the ions arising as a result of the intermolecular rearrangements, the presence of the (M + 73)† peak is characteristic of the spectra of all trimethylsilyl derivatives of organic compounds.[104–110] It has therefore been postulated[104–110] that an ion of this kind is formed as a result of the ion–molecule interaction of the trimethylsilicenium ion with the electronegative centre of the substrate molecule. These studies initiated the research into the ion–molecule reactions of trimethylsilicenium ions.

The interaction of trimethylsilicenium ions with a series of organic compounds containing various functional groups (indenamine, naphthaline, quinoline, octadec-1-ene) has been studied.[111,112] The main peak in the mass spectra of these compounds was that corresponding to the (M + 73) ion.

The investigations[111,112] established that trimethylsilicenium ions are extremely reactive species with very pronounced electrophilic properties owing to the presence of the positive charge, the unoccupied molecular *p* orbital, and the unoccupied *d* orbital. Despite the high reactivity of silicenium ions, a characteristic feature of the latter is the formation of the quasi-molecular (M + 73) complexes[111,112] and not fragment ions of the kind observed in the case of the carbenium ions. Thus the interaction of trimethylsilicenium ions with higher alcohols leads to the formation of quasi-molecular ions in 75% yield.[111] When trimethylcarbenium ions react with these alcohols, the total ionic current consists of the ionic currents of a multiplicity of fragment and quasi-molecular ions, the contribution of the quasi-molecular ion being insignificant.[130]

The investigation by the ion–cyclotron resonance method of the interaction of trimethylsilicenium ions with the alcohols ROH, where R = Me, Et, n-Pr, t-Bu, and other alkyl groups, has been reported.[113,114] It has been shown that the interaction of the silicenium ion with an alcohol molecule entails the formation of the adduct $R\overset{+}{O}H{-}SiMe_3$, which can then decompose further with loss of methane in the case of methanol and with loss of an alkene in the case of the remaining alcohols in accordance with the mechanism#

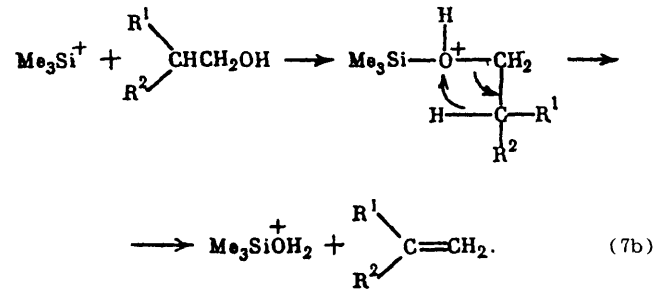




(7a)

†The mass of 73 corresponds to that of the trimethylsilicenium ion.

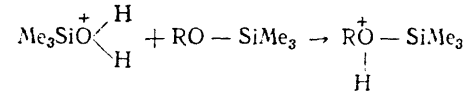
#A radiochemical study of the gas-phase reactions of dimethylsilicenium ions with methanol at a vapour pressure of the latter of 30 mmHg and that of a noble gas diluent of ~300 mmHg have shown that the only product is dimethylmethoxysilane, which is formed as a result of the proton transfer from the long-lived complex to the alcohol molecule or to the diluent gas species.[131]



(7b)

The elimination of methane in accordance with the mechanism (7a) is insignificant for higher alcohols. The explanation is apparently the stability of the alkene, which renders the process involving the elimination of the alkene rather than the methane more favourable.

It has been shown[112] that steric effects play an important role in the ion–molecule reactions in the gas phase. The (M + 73) peak was almost absent from the spectra of compounds containing a secondary siloxy-group with bulky substituents. Instead their mass spectra contained an intense (M + 1) peak. The formation of this ion can be accounted for by the interaction of the trimethylsilicenium ion with the water (atmospheric moisture) present in the system; this entails the appearance of a protonated silanol $Me_3Si\overset{+}{O}H_2$, which reacts further with a substrate molecule as a Brønsted acid, giving rise to the (M + 1) ion:



This mechanism has been confirmed by experiments using deuteriated water. In this case the (M + 1) peak shifts by unity. In addition, a peak corresponding to the protonated silanol (*m/e* 91) was present in the spectrum.

Thus, under conditions where the interaction of the fairly large trimethylsilicenium ion with electronegative atoms is hindered, the process involving the formation of the (M + 1) ion, i.e. the protonation of the substrate molecules, becomes energetically more favourable. In those cases where there is no steric hindrance in the molecule, the main reaction of the trimethylsilicenium ion is the formation of the (M + 73) quasi-molecular ion.

It follows from the analysis of data examined that, in contrast to the condensed phase, in the gas phase silicenium ions are formed readily and the relative intensities of their peaks in the mass spectra exceed by 1–2 orders of magnitude the intensities of the carbenium ions formed under analogous conditions, which agrees with the lower formation energies of the silicenium ions.

Like carbenium ions, silicenium ions have fairly pronounced electrophilic properties. The results of studies of the gas-phase ion–molecule reactions of ions of both types have demonstrated a considerable analogy in the character of their interactions and of the products formed. At the same time, by virtue of the difference between the electronic structures and properties of the carbon and silicon atoms, some differences have also been observed in the behaviour of these ions.

IV. A NUCLEAR-CHEMICAL METHOD FOR THE GENERATION OF SILICENIUM IONS AND THE STUDY OF THEIR REACTIONS

The traditional physicochemical methods proved to be unsuitable for the generation of silicenium ions in either condensed or gas phases. The mass-spectrometric and ion-cyclotron resonance spectroscopic methods make it possible to obtain these ions and to investigate their reactions but only in the rarefied gas phase. A method which permits the investigation of silicenium ions in the gas phase over a wide range of pressures and also in the liquid and solid phases has recently become available. It is based on a combination of nuclear and chemical processes: the β-decomposition of the tritium atoms forming part of the composition of the silane molecule takes place initially and this is followed by chemical changes leading to the formation of silicenium ions.

In order to understand the essential feature of the method, it is necessary to consider the β-transformation of tritium. The β-decomposition process is known to involve the transformation of a neutron into a proton in the nucleus[132] via the mechanism

$$n \rightarrow p + e^- + \tilde{\nu},$$

where n and p are the neutron and proton respectively, e^- is the nuclear electron (β-particle), and $\tilde{\nu}$ is the antineutrino. This transformation leads to the appearance of the nucleus of a new element with a charge greater by unity. Since the number of electrons in the atom remains unchanged in this process, the charge state of the resulting daughter element has increased by unity. Thus the β-decomposition of tritium can be represented schematically as follows:

$$T \rightarrow H^+ + e^- + \tilde{\nu}.$$

Since the β-particle is emitted over a period which is insignificant compared with the period of electronic vibrations, a sudden change under these conditions of the electric field of the nucleus can lead to the so-called "shaking" of the electron shell, which entails the excitation of the daughter ion.[133] In conformity with the sudden perturbation theory, this process should lead to the additional ionisation of some of the daughter ions.[134] However, for tritium, both the experimental data and calculations have shown that only 2.5% of all the transitions lead to the formation of doubly charged ions, i.e. ions with an excitation energy exceeding the second ionisation potential of helium. This is associated with a very marked intensification of the electrostatic interaction of the electron with the nucleus as a result of the doubling of the charge of the latter. Furthermore, the usual mechanism of the formation of multiply charged ions as a consequence of Auger processes does not obtain in the case of hydrogen (tritium).

The fact that the radioactive recoil energy,[133] which can also be responsible for the excitation of the ions formed, is insignificant is likewise characteristic of β-decomposition. Thus more than 90% of all the β-transformations of tritium are accompanied by a recoil energy less than 2 eV.

Thus, as a result of the β-decomposition of tritium, the yield of singly charged helium ions is a maximum compared with the yields of the ions of other elements and reaches ~97%; most of the singly charged ions (~70%) are then in the ground electronic levels or levels close to them.[134]

We shall now consider the processes occurring on decomposition of the tritium forming part of the composition of molecular systems, because these processes constitute the basis of the generation of reactive species, in particular carbenium ions.[135,136]

The first stage in the chemical changes in the β-decomposition processes of tritium atoms forming part of hydrocarbons is the appearance of primary molecular ions RHe^+. The results of theoretical and experimental studies[137-141] have shown that, as for atomic systems, most of the molecular ions formed are in the ground energy state or states close to it.

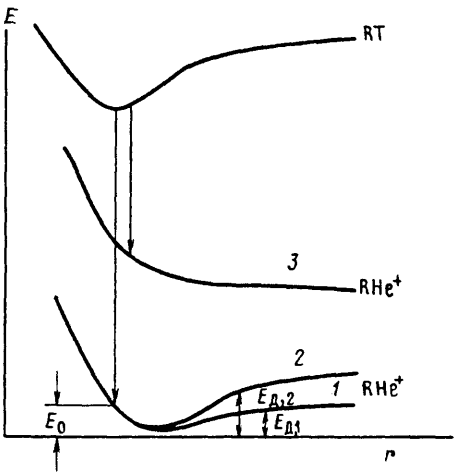


Figure 3. Potential energy curves for the RT molecule and the RHe^+ ion: *1*) and *2*) the ground state; *3*) the excited state.[140]

The configuration of the nuclei in the resulting molecular ion, which is characteristic of the initial molecular system, does not in general correspond to the minimum on the potential energy surface of this ion. According to the Franck–Condon principle, this means that the so-called vertical transitions on the potential energy diagram, associated with the change in the chemical nature and electronic state of the atoms, lead to the appearance of molecular ions in various vibrational levels. The potential energy curves for the initial molecule and the daughter ion are illustrated schematically in Fig. 3. Evidently, there can be two types of potential energy curves for the daughter ions in the ground states. In the first case the excitation energy E_0 is higher than the dissociation energy of the RHe^+ ion (curve *1*), while in the second case E_0 is lower than the dissociation energy of the RHe^+ ion (curve *2*). The first case leads to the decomposition of the primary molecular ion $RHe^+ \rightarrow R^+ + He^0$, while the second involves the retention of the RHe^+ ion.

Apart from the transitions leading to the ground states of the daughter ions, there can also be transitions resulting in excited states (curve *3*). In this case the potential energy curve has no minimum, which corresponds to a repulsion state. Such transitions inevitably lead to the dissociation of RHe^+ with formation of the R^+ ion. It has been shown[139,142,143] that the ions R^+ in the ground state do not undergo subsequent fragmentation.

The sequence of the processes developing in the β-decomposition of tritium forming part of hydrocarbons (for methane as an example) and their time characteristics have been

represented schematically as follows:

$$T_3C{:}T \xrightarrow[\sim 10^{-21}\ s]{\beta\ (a)} [T_3C{:}He^+, \beta] \xrightarrow[\sim 10^{-18}\ s]{(b)} [T_3C\cdot He^+] \xrightarrow[\sim 10^{-16}\ s]{(c)} \rightarrow$$
$$\text{(A)} \qquad\qquad \text{(B)}$$
$$\rightarrow [T_3C\cdot He^+\cdot] \xrightarrow[\sim 10^{-15}\ s]{(d)} [T_2C^+He{:}] \xrightarrow[\sim 10^{-13}\ s]{(e)} T_3C^+ + He^0.$$
$$\text{(C)} \qquad\qquad \text{(D)} \qquad\qquad \text{(E)}$$

Stage (*a*) is the transformation of the tritium nucleus into the helium nucleus, whereupon the β-particle is within the limits of the helium atom. In stage (*b*) the β-particle lies outside the limits of the molecular system, which entails the appearance of a positively charged molecular ion (B) in which the charge is localised on the helium atom. Stage (*c*) corresponds to the intra-atomic transition of the residual electron left over from the tritium atom to the energy level of the helium atom corresponding to its second ionisation potential. Stage (*d*) is the interatomic transition of an electron from the carbon atom to the helium atom—to the energy level corresponding to the first ionisation potential of this atom. The electron transfer from the hydrocarbon group to the helium atom is caused by the fact that the first ionisation potential of helium greatly exceeds (by ~15 eV) the ionisation potentials of the hydrocarbon groups. In the resulting molecular ion (D) the neutral helium atom and the charged R_3C^+ fragment become isolated. Stage (*e*) involves their separation in space, which leads to the formation of free carbenium ions. The yields of the carbenium ions obtained in this way are ~80%.[137,144]

Table 2. The probabilities *P* of the appearance of the daughter species in the ground state in the β-decomposition of a tritium atom in certain compounds.[138]

Process	*P*
$T \xrightarrow{\beta^-} He^+$	0.70
$HT \xrightarrow{\beta^-} HHe^+$	0.59
$CH_3T \xrightarrow{\beta^-} CH_3He^+$	0.61
$NH_2T \xrightarrow{\beta^-} NH_2He^+$	0.61
$OHT \xrightarrow{\beta^-} OHHe^+$	0.62

Quantum-chemical calculations[138] have shown that the nature of the initial parent form in the β-decomposition of tritium atoms does not have a significant influence on the probability of the appearance of the daughter species in the ground energy state (Table 2). It is therefore to be expected that the β-decomposition processes involving the tritium atom in the corresponding compounds of the elements in the Third Period lead to the formation of primary molecular ions whose yield in the ground energy state is close to the yield of the ions indicated in Table 2. Thus, when the tritium forming part of the composition of organosilicon compounds, in particular the substituted silanes $R_{4-n}SiT_n$, decomposes, silicenium ions in the ground energy state are formed in fairly large yields in accordance with the scheme

$$R_{4-n}SiT_n \xrightarrow{\beta} R_{4-n}Si^+T_{n-1} + He^0.$$

Thus a possibility is created for extending the nuclear-chemical method for the generation of free carbenium ions to the preparation of their silicon analogues (silicenium ions). This method of generation of silicenium ions has a number of characteristic features.

1. The silicenium ions generated by the nuclear-chemical method are formed in a free state, i.e. without a counterion and a solvation shell. The β-particle emitted on decomposition cannot serve as a counterion, because it is removed to a distance over which the interaction energy between the ion and the electron is low. The absence of a solvation shell is explained by the fact that the initial molecular system lacked such a shell and the time required for its creation after the formation of the ion exceeds by several orders of magnitude the time of the ion–molecule interactions. Such a state of the ions formed ensures their enhanced reactivity.

2. The method makes it possible to obtain, in principle, silicenium ions with the required composition and structure and with a specific localisation of the charge, because organosilicon compounds having the corresponding structure and containing tritium in the specified position can be used as the sources of such ions.

3. The rate of generation of the silicenium ions (E) is independent of external conditions (temperature, pressure, the state of aggregation, etc.), because the formation of these ions is based on radioactive decomposition processes:

$$\frac{dN(R_{4-n}Si^+T_{n-1})}{dt} = n\lambda K N(R_{4-n}SiT_n),$$

where $N(R_{4-n}Si^+T_{n-1})$ is the number of silicenium ions formed, $N(R_{4-n}SiT_n)$ the number of silane molecules, λ the decomposition constant of tritium, n the number of tritium atoms in the silane, and K a coefficient taking into account the yield of silicenium ions.

4. The given method makes it possible to generate silicenium ions and to investigate their reactions in the gas, liquid, and solid phases, since the β-decomposition processes are independent of the state of aggregation of the substance in the molecules of which tritium decomposes.

Dimethylsilicenium ions were obtained for the first time with the aid of the nuclear-chemical method via the process

$$Me_2SiT_2 \xrightarrow{\beta} [Me_2SiTHe]^+ \rightarrow Me_2SiT^+ + He^0$$

and their reactions with t-butoxydimethylsilane, pentadimethyldisiloxane, and methanol were investigated by Nefedov et al.[131] The reactions of the dimethylsilicenium ions with the compounds enumerated above are indicated schematically below:

$$\left[\begin{matrix} Me_2HSi^{\delta+}\ldots OR \\ | \\ Me_2TSi \end{matrix}\right] \rightarrow Me_2HSi^+ + Me_2TSiOR$$

$$\uparrow$$

$$Me_2TSi^+ + Me_2HSiOR \rightarrow \left[\begin{matrix} Me_2HSi\overset{+}{O}R \\ \vdots \\ Me_2TSi \end{matrix}\right]^* \rightarrow \left[\begin{matrix} Me_2HSiO\ldots R^{\delta+} \\ | \\ Me_2TSi \end{matrix}\right] \rightarrow Me_2HSiOSiTMe_2 + R^+;$$

$$Me_2TSi^+ + MeOH \rightarrow \left[\begin{matrix} Me\overset{+}{O}H \\ \vdots \\ Me_2TSi \end{matrix}\right]^* \xrightarrow{MeOH} Me_2TSiOMe + Me\overset{+}{O}H_2;$$

$R = Me_2C,\ Me_3Si.$

Further studies in this field should probably be directed to the extension of the nuclear-chemical method to the generation of other silicenium ions and to the study of their reactions with compounds of different classes in the gas and condensed phases.

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In conclusion one must state that the problem of the preparation of silicenium ions and of the investigation of their properties and reactions still remains in the stage of

development. One of the directions of this development involves the use of the nuelear-chemical method. The above discussion of the essential features of this method and of its characteristic features permits the conclusion that the method is unique, because it allows one to generate silicenium ions of different composition and structure in any substances in the gas, liquid, and solid states. The development of this method will make it possible to investigate the behaviour of silicenium ions in reactions with compounds of different classes both in the gas phase, over a wide range of pressures, and in the condensed phases.

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