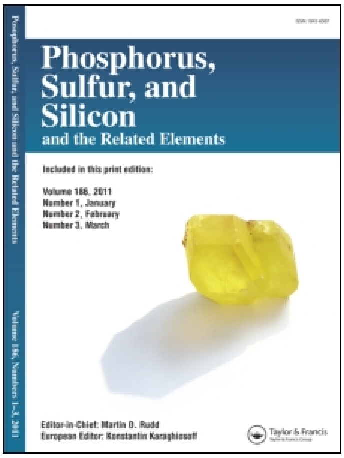

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ELIMINATION-ADDITION MECHANISMS IN SUBSTITUTION AT THE SILICON ATOM

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ELIMINATION-ADDITION MECHANISMS IN SUBSTITUTION AT THE SILICON ATOM

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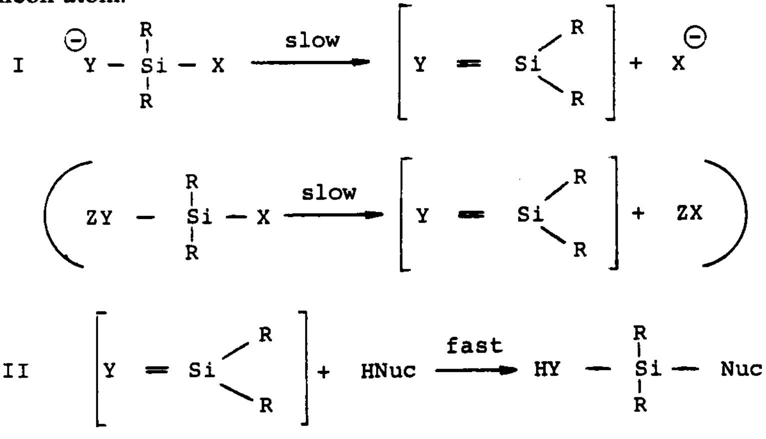
Two pathways of substitution at the silicon atom, which can be classified as elimination-addition, are discussed. One involves unsaturated tricoordinate silicon intermediate and the other sililenium ion transient species. The former mechanism reflects a similarity of silicon chemistry to the chemistry of phosphorus. In particular, metasilicate intermediates, analogues of metaphosphates may appear in some systems. On the other hand the metallic character of silicon shows up in a transient formation of the sililenium ion via the electron transfer route postulated here.

This lecture is devoted to the discussion of those mechanisms in organosilicon chemistry that involve intermediates with silicon having the coordination number three. The subject is a little controversial since silicon atom is known to have ability to expand its coordination number. Consequently penta-coordination of silicon—at least in the transition state, but possibly also in an intermediate—is a general feature of the nucleophilic displacement at silicon center. However in phosphorus chemistry the elimination-addition mechanism is rather common. Many important reactions of substitution at tetracoordinate phosphorus proceed with transient formation of metaphosphates or their analogues.[1] In the light of some known similarities of silicon and phosphorus chemistry, the question arises whether an analogous mechanism may operate in reactions of organosilicon compounds, and in particular, whether metasilicates, analogues of metaphosphates, appear as intermediates in the substitution at silicon center.

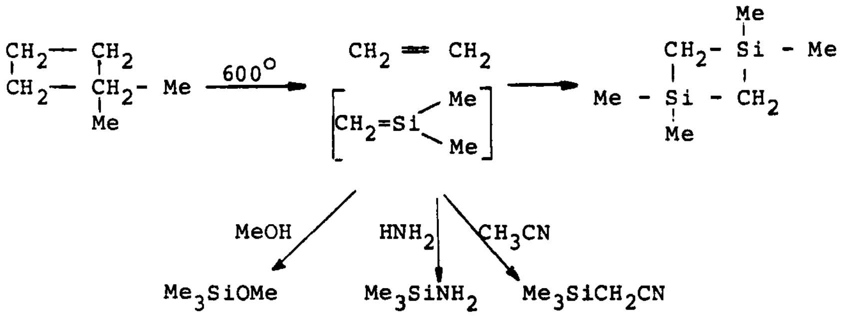
Let us first consider a more general scheme including the rate determining elimination of an anion or a neutral species from silicon leading to the formation of an unsaturated tricoordinate silicon intermediate. The addition of a nucleophile occurs in the fast consecutive step. Thus the net result is the nucleophilic displacement at silicon atom.



(1)

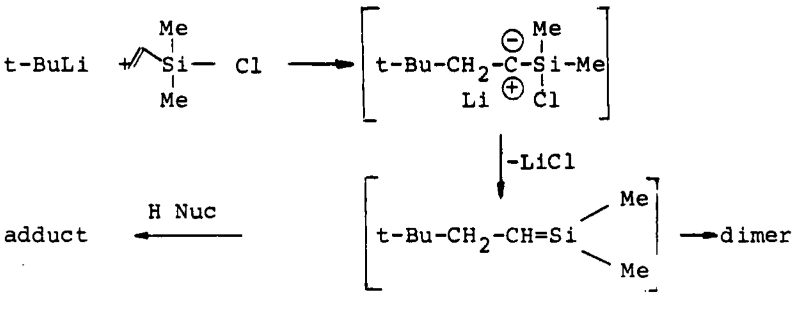
Y = C, N, O

One may consider the problem as trivial, since it is well known that many reactions at high temperatures in the gas phase proceed according to this scheme. The story started in 1966, when the transient existence of unsaturated tricoordinate silicon species was for the first time well documented by showing that dimethyl-silacyclobutane, when pyrolyzed, gives silaethylene intermediate, which may dimerize or undergo other addition processes.[1] The addition of a nucleophile may also take place, if it is present in the system.



(2)

Since that time many similar reactions have been performed. There are also many examples of the elimination-addition processes induced by irradiation, which occur at a low temperature (see for ex. ref.[3]). However, even thermally activated reactions in solution may also proceed with the transient formation of silaethylene species. It was shown[4] (Scheme 3) that the generation of a negative charge on a carbon atom adjacent to silicon also having a good leaving group attached to it (like halogen), may lead to silaethylene intermediate, which either dimerizes or possibly is attacked by a nucleophile:

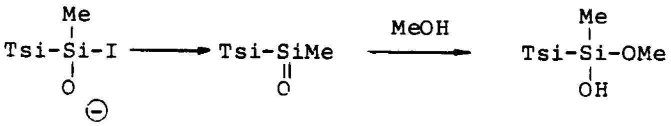


(3)

The reaction in the Scheme 3 was carried out in *n*-hexane at ambient or lower temperatures. During the last few years there have been also many examples of synthesis of stable sterically hindered compounds having tricoordinate double bonded silicon atom (see for ex. ref.[5]).

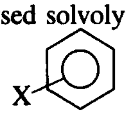
Looking now for a closer analogy to metaphosphates one may ask about intermediates having silicon-oxygen double bond. There is a body of evidence for the transient existence of these species in the gas phase. Searching for these intermediates in solution reactions has been the purpose of the joint research of Eaborn's group from Sussex (Great Britain) and our Łódź group. First, in attempting forcing a reaction to proceed via the silicon-oxygen double bond intermediate, a sterically hindered model was invoked.[6] The bulky tris-(trimethylsilyl)methyl substituent (Tsi) attached to silicon reduces markedly the ability to do S_{N^2} substitution at silicon atom. Even such an excellent leaving group as iodide in TsiSiMe(OMe)I cannot be displaced in such a strongly nucleophilic system as boiling concentrated solution of sodium hydroxide in methanol. However, if there is a possibility of formation of negative charge on oxygen bound to silicon, as in TsiSiMe(OH)I, then the displacement may be accomplished at room temperature and in a very short time.

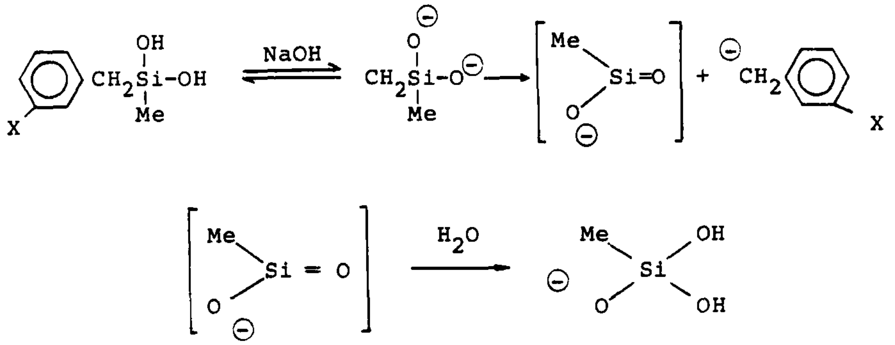
The only feasible explanation seems to be the elimination-addition mechanism involving silanone intermediate:



$$\text{Tsi-}\underset{\underset{\ominus}{\text{O}}}{\overset{\text{Me}}{\text{Si}}}\text{-I} \longrightarrow \text{Tsi-}\underset{\text{O}}{\overset{}{\text{SiMe}}} \xrightarrow{\text{MeOH}} \text{Tsi-}\underset{\text{OH}}{\overset{\text{Me}}{\text{Si}}}\text{-OMe} \quad (4)$$

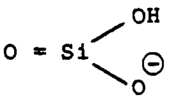
Certainly two features strongly favor the elimination-addition scheme: substantial steric effect of the substituent and a very good leaving group. However, further studies have shown that these features are not necessary to have the elimination-addition mechanism competing successfully with the S_{N^2} or the addition-elimination reaction route.

Kinetics of the base catalysed solvolytic cleavage of the benzyl group from series of compounds of the formula  $CH_2SiMe_{3-n}(OMe)_n$ $n = 1, 2, 3$ was studied in methanol-water and DMSO-water systems.[6-8] Since the methoxy group was transformed to the silanol group, the silane in the concentrated base solution was partly converted to a corresponding silanolate or in the case of substrates $n = 2$ and 3 also to silanodiolate. A considerable excess of the base over the substrate prevented condensation and simplified the kinetics making it possible to use the dependence of the specific rate on the base concentration as the diagnostic tool of the elimination-addition mechanism. The kinetic analysis led to detection and to rate evaluation of the solvolytic cleavage of the silanodiolates derived from compounds $n = 2$ and 3.[8] Since these negatively charged species are not likely to undergo any S_{N^2} or addition-elimination solvolytic process, the only feasible mechanism is the elimination-addition.

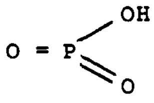


(5)

In the case of the substrate where *n* = 3, the intermediate is the anion of the hypothetical metasilicic acid I, which is isoelectronic with metaphosphoric acid II—postulated often as the intermediate in nucleophilic displacement at phosphorus atom.



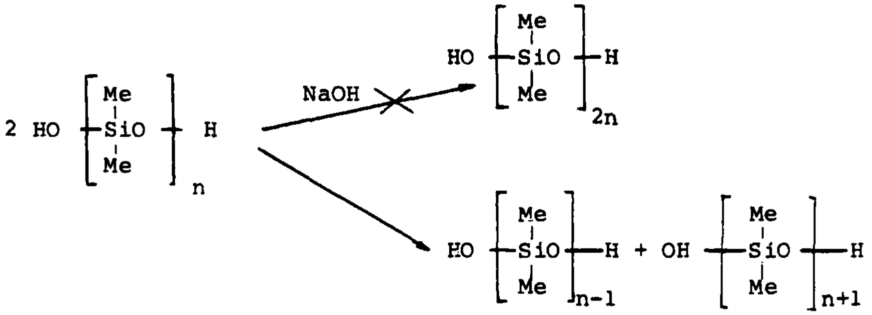
I



II

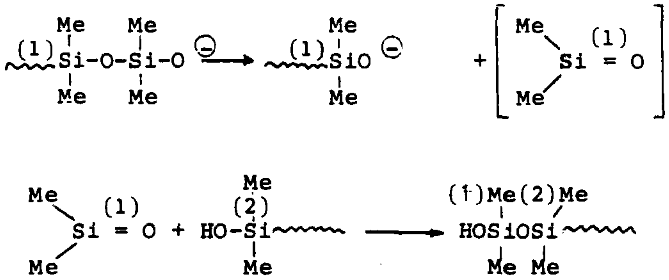
Thus the analogy to the chemistry of phosphorus is very close. Perhaps derivatives of metasilicic acids play a role of intermediates in the chemistry of silicates, which is the field now gaining a considerable importance.

The elimination-addition mechanism of the substitution at silicon atom has also some implications in the chemistry of polysiloxanes. Attempting to study base-catalysed polycondensation of linear oligosiloxanes having silanol end groups we found that instead of the expected condensation of the silanol groups, the process of the disproportionation of the oligomer chain occurs[9] according to the scheme:



(6)

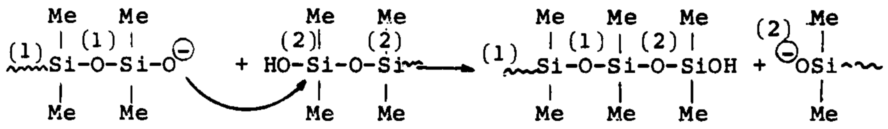
The elimination-addition mechanism (Scheme 7) seemed possible.



(7)

However the reaction could be also rationalized on the basis of an S_{N^2} mechanism, in which nucleophilic attack of the silanolate on the border silicon atom of the other molecule would lead to adjacent siloxane bond cleavage (Scheme 8).

Kinetic studies of the disproportionation process were performed for the system: $Me_3SiOSiMe_2OH$ (substrate), *i*PrONa (catalyst), *i*PrOH (solvent).[9] The reaction



$$\sim\!\overset{(1)}{\mathrm{Si}}\mathrm{Me_2{-}O{-}}\overset{(1)}{\mathrm{Si}}\mathrm{Me_2{-}O^{\ominus}} + \mathrm{HO{-}}\overset{(2)}{\mathrm{Si}}\mathrm{Me_2{-}O{-}}\overset{(2)}{\mathrm{Si}}\mathrm{Me_2}\!\sim \longrightarrow \sim\!\overset{(1)}{\mathrm{Si}}\mathrm{Me_2{-}O{-}}\overset{(1)}{\mathrm{Si}}\mathrm{Me_2{-}O{-}}\overset{(2)}{\mathrm{Si}}\mathrm{Me_2OH} + {}^{\ominus}\mathrm{O}\overset{(2)}{\mathrm{Si}}\mathrm{Me_2}\!\sim \qquad (8)$$

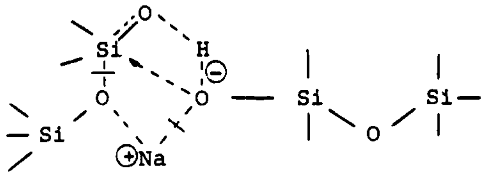
was shown to proceed bimolecularily and to have a high negative entropy of activation (-125 J. mol.$^{-1}$ deg.$^{-1}$), also no insertion of the silanone to solvent was observed at a higher concentration of the substrate. All these observations gave evidence for the S_{N^2} process represented by the Scheme 8.

However the reaction shows also some features explained better by the elimination-addition mechanism.

First of all, the silanol group must play a specific role in the cleavage of the adjacent siloxane bond. This bond is broken much faster than a siloxane bond inside the polymer chain (by a factor about 10^4). It is also strange that Si—OH bond is preserved, while neighboring siloxane bond is cleaved. Under the same conditions the nucleophilic attack directed to the border silicon atom bearing methoxy group, leads to the almost exclusive substitution of methoxide. Furthermore, the reactivity in the disproportionation is only slightly dependent on the basicity of the attacking nucleophile and the electrophilic assistance of counter-ion to the leaving group seems to play an important role.[9]

The mechanism which could account for all these observations could not be that presented by Schemes 7 or 8, but rather a borderline one—a bimolecular substitution showing some features of the elimination-addition process. We suggest that a complex of cyclic structure could be formed between silanolate and silanol (Scheme 9).

Simultaneous interaction of the anion with silanol hydrogen and the cation with the adjacent siloxane bond should lead to partial silicon-oxygen double bond and to loosening of the siloxane bond which would lead further to its cleavage.



(9)

Another type of the elimination-addition mechanism, which is considered to operate in organosilicon chemistry, is the one involving sililenium ion intermediate—analogue of carbenium ion, which appears as a transient species in the S_{N^1} mechanism in substitution at carbon atom.

$$\mathrm{R_3SiX} \xrightarrow{\text{slow}} \mathrm{R_3\overset{\oplus}{Si}} + \overset{\ominus}{\mathrm{X}}$$

$$\mathrm{R_3\overset{\oplus}{Si}} + \mathrm{Nuc} \xrightarrow{\text{fast}} \mathrm{R_3SiNu} \qquad (10)$$

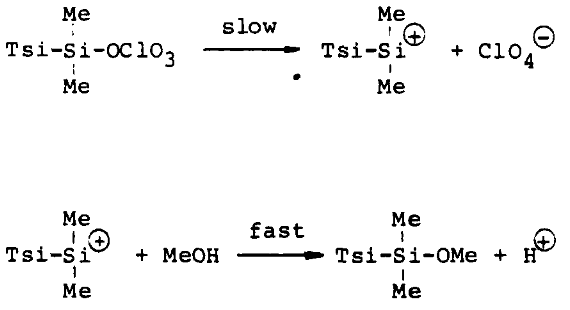
Sililenium ion—the cation having trivalent silicon with positive charge located mainly on this atom—is one of the most intriguing species in the organosilicon chemistry. There is a body of evidence of its existence in the gas phase; however, its presence in solution still remains unclear in spite of some evidence of its role as intermediate.

Numerous theoretical calculations point to stability of sililenium ions. For example, comparative calculations made for $H_3Si^{\oplus}$ ion and its carbon analogue $H_3C^{\oplus}$ showed that the former is more stable by 42 Kcal mol^{-1}(ref.[11]) and some earlier experimental estimates even gave the value at about 50 Kcal mol^{-1}.[12]

On the other hand $H_3Si^{\ominus}$ was shown to be more stable than $H_3C^{\ominus}$ also by about 50 Kcal mol^{-1},[13] which implies a considerable ability of the sililenium ion to coordinate reach in electron species. This is perhaps the reason for the difficulty in providing direct evidence of the existence of the sililenium ion in solution. Indeed, $\equiv Si^{\oplus}$ shows a great tendency to form a covalent bond with the counter-ion, which leads to a neutral species of tetravalent silicon, e.g.[14,15]. It is also prone to coordinate neutral nucleophiles much more easily than $\equiv C^{\oplus}$ does, forming thus cations with silicon of the coordination number higher than three and having the charge dispersed over other atoms (see for ex. ref.[16]). Therefore, in any attempt of generation of the sililenium ion either the application of a precursor with a considerable steric hindrance or the use of a reaction system of a very low nucleophilicity is required.

Earlier unsuccessful research aiming to provide experimental evidence for the existence of the sililenium ion in solution was reviewed by Corriu and Henner.[17] Some results of the last ten years deserve more attention. Lambert and Schulz[18] showed that tris(2-propylthio)silane, when reacted with trityl perchlorate in methylene chloride solution, gave only one product showing a high conductivity and ^1H and ^{13}C NMR spectra consistent with the sililenium ion species. However, Olah *et al.*[19] regarded that some other more convincing proofs are needed.

Indirect evidence of the sililenium ion intermediates comes from kinetic studies of Eaborn *et al.*[20] on solvolytic substitution at sterically hindered silicon atom. They showed that silyl esters of perchloric or triflic acids, also having bulky trisyl group at silicon atom, undergo solvolysis in methanol showing kinetic features of the classical S_{N^1} process.



$$\mathrm{Tsi{-}\overset{Me}{\underset{Me}{Si}}{-}OClO_3} \xrightarrow{\text{slow}} \mathrm{Tsi{-}\overset{Me}{\underset{Me}{Si}}^{\oplus}} + \mathrm{ClO_4^{\ominus}}$$

$$\mathrm{Tsi{-}\overset{Me}{\underset{Me}{Si}}^{\oplus}} + \mathrm{MeOH} \xrightarrow{\text{fast}} \mathrm{Tsi{-}\overset{Me}{\underset{Me}{Si}}{-}OMe} + \mathrm{H^{\oplus}} \qquad (11)$$

Recently chemists used the concept of the transient sililenium ion to initiate the cationic polymerization of some vinyl monomers[21] which could make possible the synthesis of various block copolymers.[22]

$$Ph_3SiCl + \overset{\oplus}{Ag}\,\overset{\ominus}{PF_6} \longrightarrow \overset{\oplus}{Ph_3Si}\,\overset{\ominus}{PF_6} + AgCl$$

$$\overset{\oplus}{Ph_3Si}\,\overset{\ominus}{PF_6} + CH_2{=}CHOR \longrightarrow Ph_3SiCH_2\overset{\oplus}{CH}(OR)\,\overset{\ominus}{PF_6} \xrightarrow{nCH_2=CHOR} \longrightarrow \text{polymer} \tag{12}$$

The main proof for intermediacy of the $Ph_3Si^{\oplus}$ species was considered the presence of aromatic groups built up at ends of the polymer chain found by the application of gel permeation chromatography using both refractive index and UV detectors. However, the exact analysis of the end group structures to confirm Si—C bond has not yet been done.

In our laboratory the dimerization of 1,1-diphenylethylene was successfully performed using a similar initiation system $R_3SiCl + Ag^{\oplus}SbF_6^{\ominus}$ R = Me or Ph.[23]

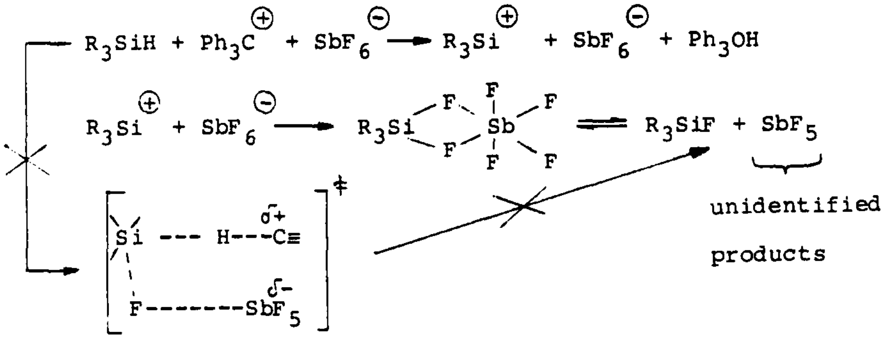
The main effort in our studies on the elimination-addition process involving the sililenium ion has been concentrated on kinetics of the reaction of silyl hydrides with carbenium ions.[24,29]

$$R_3SiH + Ph_3\overset{\oplus}{C}\,\overset{\ominus}{X} \longrightarrow R_3SiX + Ph_3CH \tag{13}$$

Earlier studies of this reaction were carried out in systems containing nucleophiles. They led to the conclusion that the process proceeded according to a synchronous mechanism.[25-27]

Our approach was the kinetic study in a system of low nucleophilicity using methylene chloride as the solvent and carbenium salt having a complex anion like $SbF_6^{\ominus}$ as the substrate. Any role of fortuitous nucleophiles, like water, was excluded by special methods of purification and preparation of the reaction solution using high vacuum technique as well as by performing control experiments with excess of water. The only two products of the reaction detected by gas-liquid chromatography were the corresponding silyl fluoride and triphenylmethane; thus the reaction may be considered as substitution of $H^{\ominus}$ by $F^{\ominus}$. In contrast with the previous mechanistic proposition we proved that the reaction proceeds by a stepwise mechanism. The first step of the process may be formally considered as hydride transfer resulting in the formation of an intermediate, which we believe to be the sililenium ion (Scheme 14).

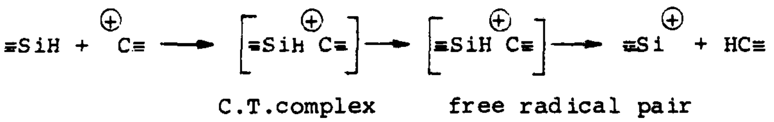
These are only consecutive reactions which eventually lead to the substitution product R_3SiF. The reaction definitely does not proceed via the synchronous transition state III. Several bits of evidence of the stepwise route were provided.[24] The first is the kinetic law. We followed the process by measuring the absorption in Vis spectrum of $Ph_3C^{\oplus}$ (435 nm.) and we found that the carbenium ion disappears at a rate proportional to the concentration of the salt even at the range of very low salt concentration, where free ions dominate over ion pairs. Certainly the second order in the salt is required for the synchronous (S_{N^2}) substitution since the rate



(14)

should be dependent on the concentration of both the anion and the cation. Furthermore it was shown that the rate of the disappearance of the carbenium ion is independent of the structure of complex anion. We checked $SbF_6^\ominus$, $BF_4^\ominus$, $SbCl_6^\ominus$ and $ClO_4^\ominus$. The $S_{N}2$ substitution rate should be dependent on the counter-ion used. It was also shown that the product, silyl fluoride, is formed with a considerable delay with respect to the disappearance of the trityl ion, while it should be formed synchronously on the $S_{N}2$ route. Finally the rate was found to be independent of the solvent polarity, though increase of the rate with decrease of the dielectric constant was expected for the $S_{N}2$ mechanism due to partial disappearance of the charge in the transition state. It is also worthy of notice that the more recent, above mentioned, Lambert's claim of successful attempt of the generation of the sililenium ion in a very similar system[18] also gives support to the scheme.

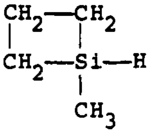
The first step in the Scheme 14 is written only formally as the hydride transfer. More detailed studies of this step seem to be of value since it represents an interesting model of a redox reaction involving silyl hydrides, which are very often used as reduction reagents in the organic synthesis. Two mechanisms could be considered: the first is the simple hydride transfer, in which hydrogen atom is moved with its electron pair from silicon to carbenium ion in one step, the other is electron transfer mechanism postulated by Kochi *et al.* for somehow similar reaction of silyl hydrides with TCNE.[28] According to this mechanism the reaction constitutes a three step process (Scheme 15). First, charge transfer complex is formed, then, in the rate limiting step, electron is transferred from the silyl hydride to the carbenium ion leading to the formation of free radical pair, which in the consecutive step collapses with the formation of the sililenium ion and triphenylmethane.



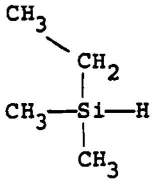
(15)

In our opinion the direct hydride transfer is very improbable and we are convinced that this is an electron transfer or a similar mechanism involving free radicals, which operates here. In order to prove it two tests were performed.[29] The first was Kochi test based on deuterium isotope kinetic effect. In the case of the direct hydride transfer there is primary isotope kinetic effect, which is expected to have rather high value. On the other hand the electron transfer mechanism should lead only to a secondary kinetic isotope effect, which is expected to be lower than 1.5. The result which we obtained lay within the limit predicted for the electron transfer route. Moreover, the values of k_H/k_D were virtually the same for trityl and tropylium ions, though these ions differ substantially in the electron affinity. Therefore the small value of the k_H/k_D should not be attributed to the unsymmetry of the transition state in the direct $H^\ominus$ transfer.

The other test[29] was based on the comparison of the rate of the reaction with the trityl ion of strained ring cyclic silyl hydride IV with its acyclic analogue V.



IV



V

Both these substrates showed almost similar reactivity, which is inconsistent with both the S_{N^2} and the direct hydride transfer. It remains, however, in accord with the electron transfer scheme.

It is worthy of notice that some other features of this reaction, like induction period observed often on the carbenium ion conversion-time curve, could not be understood on the ground of the direct $H^\ominus$ transfer mechanism either.

The electron transfer mechanism has no close analogue in the organophosphorus or sulfur chemistry. On the other hand, it reflects a similarity of the silicon chemistry to the chemistry of metals. Thus a general conclusion may be drawn that in elimination-addition processes silicon shows features typical for a metalloid center. However it exhibits also some behavior characteristic for metals.

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