Reactions of α-elimination of silanones as a path for formation and destruction of siloxane structures

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Based on modern stereoelectronic concepts, our results, and published data, we explained the paths of formation and destruction of linear and cyclic oligo- and polysiloxanes *via* intramolecular geminal decomposition of Si(OR)X groups, which results in the intermediate formation of short-lived silanones $R_2Si=O$. The latter are subsequently oligomerized, polymerized, or inserted into the Si—X bonds (X = O, Cl, *etc.*) of the trapping agents.

Key words: oligosiloxanes, polysiloxanes, geminal decomposition; silanones.

In silicon chemistry, a concept on the two most important routes for the formation of the disiloxane Si—O—Si group, which is the main unit of all siloxane structures, is predominant. These are intermolecular reactions of homo- and heterofunctional condensation (reactions (1) and (2), respectively) of organosilicon monomers and oligomers (see, *e.g.*, monographs[1–3], reviews[4,5], and literature cited herein).

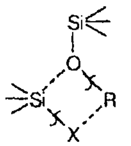
$$\gt SiOR + ROSi\lt \longrightarrow \gt SiOSi\lt + ROR \qquad (1)$$

R = H, Alk, Ac, $SiMe_3$, NO_2

$$\gt SiOR + XSi\lt \longrightarrow \gt SiOSi\lt + RX \qquad (2)$$

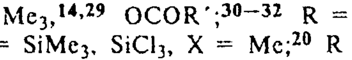
R = H, X = Cl, R'O, AcO, R_2N, H;
R = Alk, X = Cl, Br, AcO, R'_3SiO;
R = COMe, X = Cl; R = SiR'_3, X = F, Cl, Br, I;
R = Li, Na, K, X = Cl

Reactions (1) and (2) have a common mechanism. They start from the nucleophilic attack of the reagent containing the Si—O bond at the Si atom of the partner. This results in the formation of an intermediate containing the pentacoordinated Si atom. The latter is subsequently transformed into a four-membered complex, the electron transfer in which leads to decomposition with the formation of the Si—O—Si group (for reaction (1), X = OR).



It is remarkable that in the case of the heterofunctional condensation (reaction (2), where X = Cl, Br, or I; R is the hydrocarbon radical (hydrocarbyl)), the process is considerably accelerated on going from R = Me, CH_2Me, and $CHMe_2$ to CMe_3 and CH_2Ph substituents that are capable of stabilizing the carbocation. At the same time, reaction (2) does not occur when X = F.

Our studies of low-energy reactions occurring with the intermediate formation of silanones,[6–16] other works devoted to the high-temperature generation of silanones,[17–22] and analysis of extensive published data indicate that processes similar to reactions (1) and (2) can occur as intramolecular reactions when the Si atom has two geminal reactive substituents OR and X (including X = OR), resulting in the generation of the corresponding silanone according to Eq. (3).



$$\gt Si(OR)X \longrightarrow \gt Si{=}O + RX \qquad (3)$$

The R and X substituents can be the same as in Eqs. (1) and (2). For generation of silanones, silanes with the following geminal substituents* in the Si(OR)X groups were used: R = H, X = Cl, OH;[23] R is hydrocarbyl, X = I, Br,[11–14,24] Cl,[17,18,22,25] OR';[21,26] R = $SiMe_3$, $SiMe_2H$, X = I, Br,[6,7,10–14] Cl;[20] R = $SiMe_2I$(or Br), X = Cl,[27] I, Br;[6,7,12–14,28] R = COR', X = $OCMe_3$,[14,29] OCOR';[30–32] R = NO_2, X = Cl;[16] R = $SiMe_3$, $SiCl_3$, X = Me;[20] R = $S^+Me_2Cl^-$, X = Cl;[7,10–12,32] R = M^nX_{n-1} (M = Cu, Hg, Pb, Fe, and others), X = Cl, Br;[11,34–39] R = H, X is hydrocarbyl;[40] R = $Sb(OSiMe_3)_2$, X = Me;[41] R = H,[1] MgBr,[42] and X = $OSiR'_2O^-$.

In organic chemistry, the decomposition of geminal systems (*gem*-diols, α-halohydrins, α-haloesters, semiacetals, *etc.*) *via* the reaction >C(OR)X → >C=O + RX,

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* Since both of the geminal substituents OR and X are arranged in 1,1, *i.e.*, α-position, we named the decomposition of the Si(OR)X group the α-elimination reaction. However, strictly speaking, this process should be classified as the β-elimination reaction (β-decomposition), since both of the leaving substituents (R and X) are vicinal, *i.e.* arranged in position 1,2.

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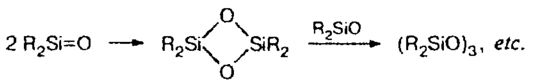
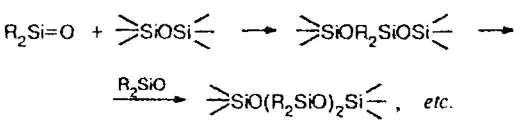
which is similar to reaction (3), has been studied long ago. The short-lived silanone appearring in a reaction of type (3), for example, dialkylsilanone $R_2Si=O$, is either cyclized to the corresponding oligocyclosiloxane according to Eq. (4), or inserted into a molecule of the reagent used as the trap or an appropriate solvent, according to Eqs. (5) and (6). Tetraorganylcyclodisiloxanes $(R_2SiO)_2$ primarily formed in the cyclooligomerization of diorganylsilanones were identified by mass spectrometry (R = Et)[8] or in the form of an insertion product in a molecule of 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane (R = Ph).[33] However, tetraorganylcyclodisiloxanes are usually very unstable[33] and react readily with diorganylsilanone to form hexaorganylcyclotrisiloxane $(R_2SiO)_3$, which is the stable product of diorganylsilanone cyclization.



(4)



(5)

$R_2Si=O + X—M \longrightarrow XR_2SiOM$ (6)

XM = OC, OSi, ClSi, HSi, OGe, ClGe, OH, ClH (see Refs. 22, 43, and 44)

Reactions (4) and (5) are the third route of formation of various siloxane structures from silanones. Generation and successive insertion of silanones into Si—O—Si units of the corresponding monomers, oligomers, and polymers according to Eqs. (4) and (5) should be considered as another scheme of formation of polymeric structures along with polyaddition and polycondensation processes. It is surprising that chemists specializing in the area of organosilicon compounds, including silanones,[17–22,43–45] were almost not interested in the geminal decomposition of the Si(OR)X group and its mechanism. Nevertheless, as far as in 1917—1919[36] and then in 1952,[23] the authors reported on the possibility of intermolecular dehydration (homofunctional geminal decomposition) of dialkylsilanediols with the intermediate formation of dialkylsilanones followed by cyclization or insertion into the Si—O—Si group (or into the H—O bond).

$$R_2Si(OH)_2 \xrightarrow[-H_2O]{} R_2Si=O \longrightarrow 1/n\,(R_2SiO)_n \qquad (7)$$

R = H,[36] Alk [23]

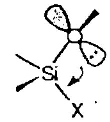
$$R_2Si=O + HOR_2SiOSiR_2OH \longrightarrow HOR_2SiOSiR_2OSiR_2OH \qquad (8)$$

However, the concepts, which were predominant in the middle of the century, that the double bond cannot exist at the Si atom forced domestic authors to forget their experimental data and the hypothesis suggested (now we can only regret this). In 1939—1942, the possibility of the existence of dialkoxysilanones $(RO)_2Si=O$ was reported.[26,46] However, these data required additional experimental support.

Let us consider stereoelectronic factors that allow the geminal decomposition of silicon compounds containing the Si(OR)X group with α-elimination of silanones. This process is favored by the so-called anomeric effect or α-effect,[47,48] which is also named n,σ*-conjugation or negative hyperconjugation.[49,50] These factors, differing in names, give qualitatively equivalent characterizations of the electron density transfer in the R—O—Si—X system and should play an important role in structures of the transition state and affect substantially the processes of geminal decomposition of these groups. The geminal interaction in the Si(OR)X fragments appears in *gauche*-conformers and is a result of the delocalization of a lone electron pair (LEP) of the O atom to the antibonding σ*-orbital of the Si—X bond. This results in the transfer of the electron density to the X atom and, in the general case, in the polarization of the Si—X bond. This electron density distribution in the Si(OR)Cl system is confirmed by the data of ^{35}Cl NQR, ^{1}H NMR, and IR spectroscopy.[51] The quantum-chemical calculations[49] of alkoxychlorosilanes also indicate that p_σ-electrons of the Cl atoms participate in the interaction considered and confirm the charge transfer from the O atom to the Si—Cl bond.

Of course, n,σ*-conjugation of the O atom in the $R'_2Si(OR)X$ molecules occurs also with the less polar Si—R′ bonds than Si—X (even if R′ is the hydrocarbon substituent). Its contribution to the electron density distribution in these molecules is less substantial, although sometimes it can affect the direction of geminal decomposition.

n,σ*-Conjugation in the Si(OR)X fragment stabilizes the conformation in which the HOMO belonging to the p-LEP of the O atom is antiperiplanar relative to the electron-accepting σ*(Si—X)-orbital.



The X atom should be more electronegative than the Si atom and less electronegative than the O atom[49,50] (X ≠ F). As the result of the n,σ*-conjugation, the Si—X bond elongates, and Si—O shortens. This effect changes the values of the bond angles at the central silicon atom and the oxygen atom bound to this Si atom. Thus, the stabilizing n,σ*-interaction occurs between the donor n-orbital of the LEP of the O atom and the acceptor antibonding σ*-orbital of the Si—X bond. In all cases, the HOMO is stabilized (the energy decreases, and the ionization potential increases) by the n,σ*-interaction. The destabilizing interaction takes place between the occupied n-orbital of the O atom and the occupied σ-orbital of the Si—X bond. Due to the n,σ-interaction, the energy of the HOMO increases, and the ionization potential decreases.

The substantial effect of the n,σ-interaction on the stereoelectronic structure of a molecule of the $R'_2Si(OR)X$ type is confirmed by both the quantum-chemical calculations and experimental results.[49,50]

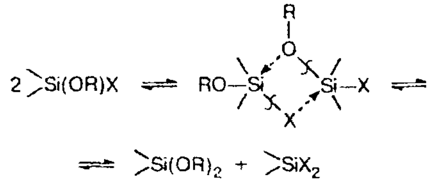
We also suggested[47] an alternative explanation of the electron density distribution in the Si(OR)X system: the Coulomb interaction of the O atom charge directly through the field with the electron of the Si—X bond.

For α-elimination of silanones, the substituent bound to the O atom in the Si(OR)X group should exhibit at least weak electrophilic properties. The nucleophilic attack of the X atom to the C atom, to which the siloxane oxygen is bound, occurs especially easily when it exists in the sp^3-hybridization state and has the smallest electron charge. The R—X bond is formed by overlapping of the HOMO of the nucleophile X with the LUMO of the O—R bond (the transition state appears due to mixing of these orbitals). When R is a hydrocarbon radical capable of forming a substantially stable carbocation ($R = CMe_3$, $CH_2CH=CH_2$, or $CH_{3-n}Ph_n$, where $n = 1-3$, *etc.*), the cleavage of the O—R bond during the geminal decomposition of this group occurs sufficiently easily. For example, α-elimination of dichlorosilanone from benzyloxytrichlorosilane proceeds smoothly at 500—650 °C.[18]

$$Cl_3SiOCH_2Ph \xrightarrow{\Delta} Cl_2Si=O + ClCH_2Ph \qquad (9)$$

By contrast, trichloromethoxysilane is stable at 700 °C. At this high temperature, Cl_3SiOMe does not form even traces of MeCl and disproportionate to $(MeO)_2SiCl_2$ and $SiCl_4$ only by 5%.[52]

Therefore, it should be emphasized that organosilicon compounds containing the Si(OR)X group, where R is hydrocarbyl and X is halogen (alkoxyhalosilanes, alkylalkoxyhalosilanes, *etc.*), can represent two directions of geminal decomposition: (1) intramolecular α-elimination of the corresponding silanone according to Eq. (3); (2) intermolecular reversible disproportionation (equilibrium redistribution of substituents) according to Eq. (10),[1,53] which does not result in the formation of the SiOSi group.



$$2\,{>}Si(OR)X \rightleftharpoons [RO{-}Si(\mu\text{-}OR)(\mu\text{-}X)Si{-}X] \rightleftharpoons {>}Si(OR)_2 + {>}SiX_2 \qquad (10)$$

Reaction (10) proceeds *via* the four-membered transition state with the pentacoordinated Si atoms and can be illustrated by the simple example:[1]

$$2\,(RO)SiCl_3 \rightleftharpoons (RO)_2SiCl_2 + SiCl_4. \qquad (11)$$

The ability of alkoxyhalosilanes to disproportionate according to Eq. (10) increases as the atomic number decreases and the halogen nucleophilicity increases, whereas their tendency to geminal decomposition according to reaction (3) changes in the inverse order. Reaction (10) occurs especially easily when X = F (already at 20 °C); when X = Cl, the reaction occurs under more drastic conditions (100—200 °C). The rate of rearrangement of alkoxyfluorosilanes $(RO)_{4-n}SiF_n$ (R = Me or Et) increases when the number of F atoms (*n*) in the molecule increases. Compounds of this series with *n* = 2 and 3 disproportionate readily even at temperatures close to room temperature.[54—59] For example, $MeOSiF_3$ disproportionates at −40 °C to form mainly $(MeO)_4Si$ and SiF_4.[55]

Alkoxyfluorosilanes and alkoxyfluorodimethylsilanes are very unstable due to the different electron density distribution in the Si(OR)F group as compared to that in Si(OR)Cl, which is evidenced, in particular, by the IR spectroscopy data for $Me_2Si(OR)X$ (X = F or Cl)[56] and an increased nucleophilicity of the F atom with respect to the Si atom.

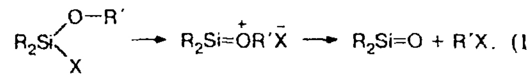
Alkoxybromo- and bromophenoxysilanes are poorly studied,[46,57] and their disproportionation was not observed. Bromotriethoxysilane was assumed[46] to decompose with elimination of diethoxysilanone.

$$(EtO)_3SiBr \longrightarrow (EtO)_2Si=O + EtBr \qquad (12)$$

To date, alkoxyiodosilanes are unknown (see below).

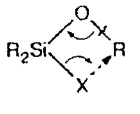
It is known that aroxychlorosilanes can disproportionate. In particular, this has been shown for chlorodimethylphenoxysilane.[58] However, attempts at disproportionation of chlorodiphenylphenoxysilane were unsuccessful.[58]

Generation of silanones from the $R_2Si(OR')X$ molecules was suggested[42] to occur according to the following scheme:



$$R_2Si(OR')X \longrightarrow R_2Si{=}\overset{+}{O}R'\,\overset{-}{X} \longrightarrow R_2Si{=}O + R'X. \qquad (13)$$

In our opinion, it is more probable that the reaction occurs *via* the four-centered state followed by electron density transfer without charge separation, which results in a decrease in the activation energy of the geminal decomposition and α-elimination of the corresponding silanone).



Compounds containing a highly electrophilic substituent ($R = SiF_3$, H, nonsubstituted or substituted metal cation, and others) and (or) easily polarizing Si—X bond (for example, at X = I) are most prone to geminal decomposition according to reaction (3).

When the R substituent in the Si(OR)X fragment is an inactivated aromatic group (for example, Ph), these systems usually exhibit no geminal decomposition. This is due to the higher stability and order of the O—Ar bond.

Geminal decomposition of the Si(OR)X systems proceeds especially readily when R is a metal ion or a metal-containing cation (for example, MgBr, HgCl, *etc.*). Intermediate products containing such geminal fragments as $Si(OM^{n}X_{n-1})X$ (M is the *n*-valence metal, X = Cl, Br, or I) are formed when H_2SiX_2 or R_2SiX_2 react with metal oxides[11,34–39,60] and in reactions of organomagnesium compounds with oligodimethylsiloxane-α,ω-diols or permethylcyclosiloxanes.[1,42]

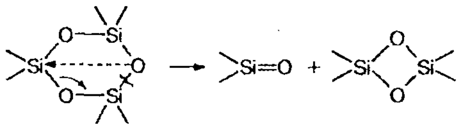
As early as in 1961, based on the X-ray structural data on silicates, we have shown[61] for the first time that in the geminal $(Si)OSi-O^{-}M^{+}$ systems, the $Si-O^{-}M^{+}$ bond is shorter (1.50—1.60 Å) and the (Si)O—Si bond is longer (1.70—1.88 Å) than the standard interatomic Si—O distance (1.64 Å). This indicates an increased order (double bonding) of the Si—OM bond, *i.e.*, "pre-existence" of the >Si=O group, and an increased ion character of the (Si)O—Si bond, which corresponds to the modern concepts on the electron density distribution in the Si(OR)X system.

The partial double bonding of the Si—O bond in alkali trimethylsilanolates is also evidenced by the average value of its length (~1.60 Å).[1] In the (Si)O—Si—OM group, the Si—O(M) bond order decreases, and the ionicity of the (Si)O—Si bond increases along with an increase in the dynamic coefficient and, most likely, an increase in the Si—O(M) bond order. The Si—O—Si angle decreases by 8—10°, which favors geminal decomposition. These conclusions were supported by spectroscopy.[62–64] The higher Si—O bond order in alkali trimethylsilanolates was established[63] by ^1H NMR spectroscopy. Due to the higher Si—O bond order, in the IR spectra of alkali trimethylsilanolates,[63,64] the frequencies of antisymmetrical stretching vibrations of the Si—OM bond increase on going from M = Li to M = Cs. In the IR spectra of tetramethyldisiloxane-1,3-diol and its silanolates $MOMe_2SiOSiMe_2OM$, the frequencies of antisymmetrical and symmetrical vibrations of Si—O—Si decrease on going from M = H to M = Li, Na, and K.[62] The IR spectrum of sodium trimethylsilanolate and the calculation of the frequencies and shapes of vibrations of the molecule indicate that the $SiO^{-}-Na^{+}$ bond is predominantly ionic.[62]

According to Eq. (3), the formation of silanones due to the geminal decomposition proceeds especially readily if the Si atom in the Si(OR)X fragment is bound to a sufficiently electronegative X atom with a lone electron pair. An increase in the atomic radius of X, length and polarizability of the Si—X bond and, hence, a decrease in its energy facilitate the decomposition. This is especially pronounced for X = I, because the I^{-} anion is the most easily leaving one among halide ions.

The fluorine atom has an opposite (as compared to other X substituents) effect.* The Si—O bond length is still shortened (1.56—1.58 Å) in $MeOSiF_3$ and $F_3SiOSiF_3$ most likely due to the strong −*I*-effect of the F atoms, and the polarity of the O—R bond is higher. Therefore, α-elimination of silanones from the geminal Si(OR)F systems occurs only when R is a sufficiently efficient electrophile (R = $SiMe_{3-n}F_n$ (*n* = 1—3),[28,59,67–69] BF_2,[28] metal ion, and others). This geminal decomposition is characteristic of the Si—O—Si—F systems, since the F atom is the strongest nucleophile with respect to the Si atom. In particular, we observed stable Si—F→Si bridges by IR spectroscopy.[70]

Thermal destruction of peralkylcyclosiloxanes begins from the α-elimination of dialkylsilanone.[1,43,44,71–73] This process for $(R_2SiO)_3$ can be presented by Eq. (14)



(14)

or in the general form

$$(R_2SiO)_n \xrightarrow[-R_2Si=O]{\Delta} (R_2SiO)_{n-1} \xrightarrow[-R_2Si=O]{} (R_2SiO)_{n-2},\ etc. \quad (15)$$

Equation (14) explains the fact that hexamethylcyclotrisiloxane D_3 is most stable in thermolysis of permethylcyclosiloxanes D_n.[71–73] At first glance this fact is surprising because the planar strained cycle D_3, which exists in one conformation, is the most reactive one in heterolytic reactions among all permethylcyclosiloxanes (except D_2). Lower energies of the Si—O bonds in D_3 as compared to those in D_4 and D_5 (104.4, 105.9, and 106.6 kcal mol^{-1}, respectively) correspond to this situation.[74]

The hindered character of the geminal decomposition of peralkylcyclotrisiloxanes according to Eq. (14) is due to their conformational rigidity (nonflexibility of the cycle), which prevents the formation of a four-centered transition state preceding α-elimination of dialkylsilanone. Tetramethylcyclodisiloxane D_2 that is formed along with $Me_2Si=O$ during thermolysis of D_3 is very unstable and immediately decomposes to two molecules of dimethylsilanone. The latter inserts into the Si—O bonds of the D_2 molecule (to form D_3) or molecules of D_3, D_4, D_5, *etc.*:

$$(Me_2SiO)_3 \underset{+Me_2Si=O}{\overset{-Me_2Si=O}{\rightleftharpoons}} (Me_2SiO)_2 \rightleftharpoons 2\ Me_2Si=O, \quad (16)$$

$$Me_2Si=O + (Me_2SiO)_n \longrightarrow (Me_2SiO)_{n+1}. \quad (17)$$

The Si—O bond in cyclosiloxanes is very stable toward homolytic cleavage,[1] and their splitting to biradicals $^{\cdot}SiR_2(OSiR_2)_nO^{\cdot}$ is unreal.

The destruction of very thermostable hexamethyldisiloxane occurs very slowly at 500 °C (conversion

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* According to the rule formulated in Ref. 65, in the geminal Y—C—X systems, the electron density is shifted from the more electronegative Y atom to the less electronegative X atom; conversely, in the vicinal Y—C—C—X systems it is shifted from the X atom to Y. This regularity was convincingly confirmed by the data of ^{35}Cl NQR,[65] vibrational and electron spectroscopy, and quantum-chemical calculations.[66]

~5%) with intermediate α-elimination of dimethylsilanone according to Eq. (3) ($R = SiMe_3$, $X = Me$) and formation of linear permethyloligosiloxanes and tetramethylsilane[73] (Eqs. (18) and (19)).

$$\mathrm{Me_3SiOSiMe_3 \xrightarrow{500\ ^\circ C} Me_2Si{=}O + SiMe_4} \qquad (18)$$

$$\mathrm{Me_3SiOSiMe_3} + n\ \mathrm{Me_2Si{=}O} \longrightarrow \mathrm{Me_3SiO(Me_2SiO)}_n\mathrm{SiMe_3} \qquad (19)$$

(n = 1—3)

The formation of $Me_2Si=O$ and $SiMe_4$ by the thermolysis of $Me_3SiOSiMe_3$ was confirmed in Ref. 20. The decomposition of hexamethyldisiloxane in plasma occurs similarly to form permethyloligosiloxanes and $SiMe_4$, although the authors of Ref. 75 suggest a different and less probable, in our opinion, scheme for this process. The degree of thermal decomposition of low-molecular-weight linear permethylsiloxanes $Me_3Si(OSiMe_2)_nMe$ (n = 1—6) increases with an increase in n. This process results in the formation of all the lowest permethyloligosiloxanes down to n = 1,[4,76] $SiMe_4$ (n = 0), and permethylcyclosiloxanes $(Me_2SiO)_m$ (m = 3—6). The formation of the thermolysis products listed above can be explained only by the intermediate generation of dimethylsilanone, its subsequent insertion into the Si—O—Si groups, and oligomerization, as has been established for the thermal decomposition of permethylcyclosiloxanes.[1,43,44,71–73] However, the rate and character of thermal destruction of high-molecular-weight permethylpolysiloxanes (n = 30—100) are almost independent of the macromolecule length,[77–80] which can be explained by the very low content of terminal methyl groups.

The previously suggested[73] free-radical mechanism of thermal destruction of hexamethyldisiloxane, permethyloligosiloxanes, and permethylcyclosiloxanes with the homolytic cleavage of the Si—O bonds cannot be considered as correct. Nevertheless, the authors of Ref. 73 could not explain the scheme of thermal decomposition of linear permethyloligosiloxanes without accepting the possibility of the intermediate formation of dimethylsilanone. They designated this species as the biradical $Me_2Si^{\cdot}O^{\cdot}$. This study,[73] which had demonstrated for the first time the possibility of the intermediate formation of dimethylsilanone (although it was not indicated by the authors), should be recognized as pioneering. It was assumed[81] that the decomposition of the polydimethylsiloxane chains under ultrasonication occurs *via* the molecular mechanism without the participation of macroradicals and involves the generation of the terminal silanone groups —(Me)Si=O.

Thermal decomposition (depolymerization) of oligo- and polyalkylsiloxanes containing one or two terminal silicon-functional substituents X is of special interest. Their destruction with the intermediate formation of dialkylsilanone due to the geminal decomposition of the terminal $OSiR_2X$ groups can occur under mild conditions rather than at high temperatures depending on the nature of X. For example, it has been established[42] in 1960 that the reactions of oligodialkylsiloxane-α,ω-diols with organomagnesium compounds of the acetylene series occurs stepwise with intermediate formation of dialkylsilanones according to Eqs. (20) and (21).

$$\mathrm{HO(R_2SiO)}_n\mathrm{H} \rightleftharpoons \mathrm{HO(R_2SiO)}_{n-1}\mathrm{H} + \mathrm{R_2Si{=}O} \qquad (20)$$

$$\mathrm{R_2Si{=}O + R'MgX \longrightarrow R_2R'SiOMgX \xrightarrow{H_2O} R_2R'SiOH + HOMgX} \qquad (21)$$

For example, the decomposition of $HO(R_2SiO)_{n-1}H$ or peralkylcyclosiloxanes occurs consecutively according to the scheme indicated to form (n – 1) molecules of $R_2Si=O$, which react with R'MgX.

The same authors[42] mentioned the difference of the terminal Si—O—Si group from the internal groups in the oligodialkylsiloxane-α,ω-diol molecules. In their opinion, in the $\mathrm{HO{-}[R_2SiO]_{n-3}{-}(R_2SiO)_2{-}R_2SiOH}$ molecule, the effect of d_π—p_π-conjugation in the Si—O—Si group is changed due to the influence of the hydroxyl R_2Si—OH group. This weakens the terminal Si—O bond and favors the migration of hydrogen over the site of the Si—O bond cleavage and the elimination of dialkylsilanone from the molecule. At the same time, the authors of Ref. 42 did not rule out that the terminal silanol groups could interact with an organomagnesium reagent to form the SiOMgBr group, which indeed should take place. These concepts[42] were sufficiently progressive for that time.

The initial rate of thermal destruction of polydimethylsiloxane-α,ω-diols decreases as their molecular weight increases, *i.e.*, when the content of terminal hydroxyl groups in the polymer decreases. Hexamethylcyclotrisiloxane[1] (the primary stable product of the dimethylsilanone cyclization) is the only product of the thermolysis *in vacuo*. The thermal destruction of polydimethylsiloxane-α,ω-diols in the presence of water vapor, which prevents intermolecular anhydrocondensation according to Eq. (1), also favors their depolymerization.

The appearance of insignificant amounts of methane during the thermolysis of permethylpolysiloxane-α,ω-diols $HO(Me_2SiO)_nSiMe_2OH$ can also be explained by the geminal decomposition with the formation of the terminal —OSi(=O)Me group. The rate of destruction of α,ω-disubstituted polydimethylsiloxanes $X(Me_2SiO)_nSiMe_2X$ depends substantially on the nature of terminal substituents X.[1,4,80] This is supported by the fact that the replacement of the terminal hydroxyl groups in polydimethylsiloxane-α,ω-diols by methyl groups 30—35-fold decreases the thermal destruction rate of these polymers.[4,78] The initial rate of the destruction process simultaneously increases from 350—370 °C to 390—420 °C.

Thermostable terminal substituents block polydimethylsiloxane macromolecules (X = Me, Ph, *etc.*), and the chain breakage with elimination of dimethylsilanone can also occur in its internal regions through the four-centered transition state similarly to that described above for permethylcyclosiloxanes. Only this fact can explain the formation of permethyloligocyclosiloxanes $(Me_2SiO)_n$ (n = 3—10) as the products of thermolysis of linear permethylpolysiloxanes. Their formation due to the homolytic cleavage of two Si—O bonds in certain parts of the polysiloxane chain is improbable. The stability of the Si—O—Si group to homolytic cleavage is indicated, in particular, by the fact that peralkylcyclosiloxanes cannot polymerize under the action of free-radical initiators and that their radiation polymerization (γ-irradiation with ^{60}Co) is very difficult. The radiation process occurs *via* the ionic mechanism, and its rate is not affected by the presence of diphenylpicrylhydrazyl.[1] Finally, if thermal destruction of linear and cyclic permethylsiloxanes occur *via* the free-radical mechanism, methyl radicals would be the primary products of the homolytic decomposition, because the Si—C bond energy is considerably lower than the Si—O bond energy (72 and 105 kcal mol^{-1}, respectively). Presently, it is convincingly proved that no thermal dissociation of the Si—O bonds, which are very stable toward homolytic cleavage, occurs during depolymerization of polydialkylsiloxanes.[79,80] Destruction of polydimethylsiloxane chains due to the intramolecular coordination of the Si and O atoms separated by more than two O—Si groups is also improbable, because it is difficult to bring together such remote centers of the macromolecule.

All available experimental data indicate that the thermal destruction of linear polydialkylsiloxanes begins from the ends of the polysiloxane chain and occurs according to the scheme of avalanche-like geminal decomposition of the terminal $SiOSiR_2X$ groups with α-elimination of dialkylsilanone (according to Eq. (22)) propagating along the chain ("effect of falling dominoes") up to the formation of the final product $XSiR_3$ (n = 0).

$$X(R_2SiO)_nSiR_3 \xrightarrow[-R_2Si=O]{} X(R_2SiO)_{n-1}SiR_3 \xrightarrow[-R_2Si=O]{} X(R_2SiO)_{n-2}SiR_3,\ etc. \qquad (22)$$

Depending on the nature of the terminal substituents X, which are the initial active centers of depolymerization of α,ω-difunctional polydialkylsiloxanes,[79,80] the rate of thermal decomposition of $X(R_2SiO)_nSiR_2X$ decreases in the following series of X: M (K, Na, or Li) > OSO_3H > OH > Me > Ph.[1]

Anionic and cationic polymerization of peralkylcyclosiloxanes, their depolymerization, and equilibrium distribution reactions, regardless of the nature of the ionic catalyst, occur with cycle opening and the intermediate formation of an α,ω-difunctional oligomer with the same number of silicon atoms (Eq. (23)).

$$(OSiR_2)_n + X^+Y^- \longrightarrow X(OSiR_2)_{n-1}OSiR_2Y \qquad (23)$$

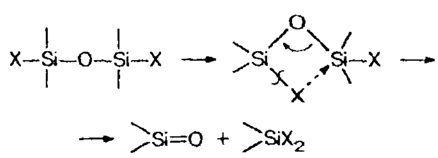
Since these α,ω-difunctional oligo- and polydialkylsiloxanes easily decompose according to Eq. (22) with α-elimination of dialkylsilanones, it should be assumed that the latter play an important role in these transformations of peralkylcyclosiloxanes. This is completely supported by many experimental data generalized in reviews (Refs. 1 and 4), and they cannot be considered in the framework of this work.

It is noteworthy that α,ω-difunctional polymers and oligomers are formed by thermolysis of polydialkylsiloxanes containing admixtures of basic or acidic polymerization catalysts. This is the reason for a lower thermal stability of these silicon-containing polymers. Ionic catalysts cleave Si—C bonds rather than terminal and internal Si—O—Si groups to form silicon-functional substituents X = OH, ONa, OK, OSO_3H, *etc.*[1,79]

The mechanism of destruction of α,ω-difunctional oligo- and polydialkylsiloxanes with the intermediate formation of dialkylsilanones is convincingly confirmed for the first terms of the homological series of $X_nR_{3-n}SiOSiR_{3-n}X_n$ (n = 1—3). Their geminal decomposition can be presented by the general equation

$$X_nR_{3-n}SiOSiR_{3-n}X_n \longrightarrow X_{n-1}R_{3-n}Si{=}O + X_{n+1}SiR_{3-n}. \qquad (24)$$

Reaction (24) evidently occurs through the four-centered transition state.



(25)

It proceeds especially readily when X = F and I. However, the electron density distributions in the transition states differ due to a sharp difference between the electronegativities of the F and I atoms and nucleofugic abilities of their anions. At the same time, the similar decomposition of oligodialkylsiloxanes with X = Cl and Br occurs only at high temperatures or under the catalytic action of Lewis or Brönsted acids. Coordinating at the O atom of the siloxane fragment, these acids polarize (and thus weaken) the Si—O bond to enhance the electrophilicity of the S atom, which facilitates the decomposition according to Eq. (25).

According to the aforesaid, the thermal stability of hexahalodisiloxanes, their closest homologs $X_3Si(OSiX_2)_nX$, and cyclic analogs $(X_2SiO)_n$ depends substantially on the nature of the halogen atom X. Fluorosubstituted disiloxanes are thermally unstable, and their lability increases as the number of F atoms in the molecule increases.

For example, hexafluorodisiloxane and octafluorotrisiloxane are very unstable and decompose easily even at room temperature to form SiF_4 and SiO_2.[67—69] Similarly, the geminal decomposition of ethylpentafluorodisiloxane at 130 °C gives polyethylsilasexquioxane $(C_2H_5SiO_{1.5})_n$ and SiF_4. 1,1,3,3-Tetrafluoro-1,3-diorganyldisiloxanes decompose easily according to Eq. (24) to form the corresponding trifluoroorganylsilane.[69]

Under similar conditions, 1,1,3,3-tetrafluoro-1,3-dimethyl- and 1,3-diethyl-1,1,3,3-tetrafluorodisiloxanes are transformed into the corresponding alkyltrifluorosilanes and polymer, while 1,1,3-triethyl-1,3,3-trifluorodisiloxane is transformed into Et_2SiF_2 and 1,1,3,3-tetraethyl-1,3-difluorodisiloxane. The latter can be considered as the product of insertion of $Et_2Si{=}O$ into the Si—F bond of the Et_2SiF_2 molecule. At the same time, pentaethylfluorodisiloxane is stable even at temperatures >110 °C. All alkylfluorodisiloxanes mentioned are the products of the reactions of the corresponding chlorosubstituted derivatives with NH_4F. 1,3-Difluoro-1,1,3,3-tetramethyldisiloxane decomposes slowly but completely even at room temperature to form $(Me_2SiO)_3$ (the product of trimerization of $Me_2Si{=}O$) and Me_2SiF_2.[28] The geminal decomposition of the very labile 1,1,3,3-tetrafluoro-1,3-dimethoxydisiloxane gives $MeOSiF_3$, $(MeO)_2SiF_2$ and polymeric products.[69]

Hexachlorodisiloxane and alkylchlorodisiloxanes, unlike isostructural fluorosubstituted derivatives, are very thermostable. Hexachlorodisiloxane and octachlorotrisiloxane decompose only at 500—1000 °C according to Eq. (24) to form $SiCl_4$ and linear and cyclic perchlorooligosiloxanes[82] (with the intermediate formation of dichlorosilanone). At higher temperatures (>1000 °C), $SiCl_4$ and SiO_2 are the products of their thermolysis.[83]

In the presence of tertiary amines, the geminal decomposition of hexachlorodisiloxane occurs slowly in the same direction already at its boiling point (136 °C).[82,84,85] The reaction mechanism suggested in these works includes the initial stage of the process that does not stand up under scrutiny:[84]

$$R_3N + Cl_3SiOSiCl_3 \rightleftharpoons R_3N^+SiCl_3 + OSiCl_3^- . \qquad (26)$$

The catalytic action of tertiary amines on the disproportionation of hexachlorodisiloxane (and its homologs as well) is based on the primary formation of their adduct containing the pentacoordinated Si atom. This results in the shift of the electron density to the O and Cl atoms to facilitate the subsequent geminal decomposition.

$$R_3N + Cl_3SiOSiCl_3 \longrightarrow Cl_3(R_3N)SiOSiCl_3 \longrightarrow Cl_2Si{=}O + R_3N + SiCl_4 \qquad (27)$$

The thermolysis of 1,1,1-trichloro-3,3,3-trimethyldisiloxane occurs in two directions with α-elimination of dichlorosilanone and dimethylsilanone.[20]

$$\begin{tikzcd}
Me_3SiOSiCl_3 \arrow[r, "a"] \arrow[dr, "b"'] & Me_2Si{=}O + MeSiCl_3 \\
& Cl_2Si{=}O + Me_3SiCl
\end{tikzcd} \qquad (28)$$

These silanones were detected as the products of insertion into the starting $Me_3SiOSiCl_3$ ($Me_3SiOSiCl_2OSiCl_3$ and $Me_3SiOSiMe_2OSiCl_3$) and into $Me_3SiOSiMe_3$ used as the trap ($Me_3SiOSiCl_2OSiMe_3$ and $Me_3SiOSiMe_2OSiMe_3$, respectively). In our opinion, the scheme suggested in Ref. 20 (Scheme 1) is improbable.

Scheme 1

$$\begin{tikzcd}
Me_3Si^{\cdot} + {}^{\cdot}OSiCl_3 \arrow[r, shift left] \arrow[d] & Me_3SiOSiCl_3 \arrow[l, shift left] \arrow[r, shift left] & Me_3SiO^{\cdot} + {}^{\cdot}SiCl_3 \arrow[l, shift left] \arrow[d] \\
Me_3SiCl + Cl_2Si{=}O & & Me_2Si{=}O + MeSiCl_3
\end{tikzcd}$$

As shown above, the homolytic cleavage of the Si—O bond is very difficult, and less stable Si—Me bonds should cleave first under the conditions studied.

1,1,3,3-Tetraalkyl-1,3-dichlorodisiloxanes $(ClR_2Si)_2O$ (R = Me or Et) decompose under prolonged heating at 175 °C according to Eq. (24) to form R_2SiCl_2 and $(R_2SiO)_3$.[27]

Hexabromodisiloxane is considerably less stable than hexachlorodisiloxane. Being refluxed for a long time (200—260 °C), it decomposes slowly to $SiBr_4$, $Br(Br_2SiO)_nSiBr_3$ (n = 2—4), and SiO_2. At higher temperatures, dodecabromopentasiloxane (n = 4) is not formed.[68,86,87] Hexaiododisiloxane $I_3SiOSiI_3$ is unknown and can hardly exist under normal conditions because of the decomposition to SiI_4 and SiO_2.

The thermal decomposition of hexahalodisiloxanes to the corresponding tetrahalosilane and silicon dioxide can be presented as follows:

$$X_3SiOSiX_3 \longrightarrow X_2Si{=}O + SiX_4, \qquad (29)$$

$$2\,X_2Si{=}O \longrightarrow X_3SiOSi({=}O)X \longrightarrow SiX_4 + SiO_2, \qquad (30)$$

X = Cl, Br, I.

It is quite possible that labile tetrahalocyclodisiloxane is an intermediate product of this reaction.

The concepts developed in this work are based on the results of our studies of compounds containing Si—I bonds.[6,84—95] In particular, we have observed for the first time the capability of iodosilanes to cleave easily COC, COSi, and SiOSi fragments. We repeatedly attempted to synthesize and isolate organosilicon derivatives containing ISiOC and ISiOSi fragments, for example, $ISi(OEt)_3$, $Me_2Si(OEt)I$, $IMe_2SiOSiMe_3$, or $IMe_2SiOSiMe_2I$, but always failed. Other researchers also failed to synthesize organosilicon compounds containing SiOSiI and COSiI groups. All studied reactions in which these substances should presumably be formed always resulted only in products of their geminal decomposition. Attempts to obtain alkoxyiodosilanes containing the Si(OR)I group by the reactions of tetraalkoxysilanes with PI_3 and HI were unsuccessful.[46,96]

Alkyl iodide and polymers were the products of these reactions. Alkoxychlorosilanes were also not transformed into the corresponding alkoxyiodosilanes.[97] The reactions of alkoxysilanes $ROSiH_3$ (R = Me, Et) with iodine or mercury iodide did not give alkoxyiodosilanes as well.[98] Nevertheless, the possibility of the intermediate formation of alkoxyiodosilanes was assumed.[46,96,97,99] It was indicated that even unstable iodotriethoxysilane most likely exists at temperatures <30 °C. [97] At the same time, iodotriphenoxysilane is thermally stable. It was even distilled *in vacuo* (9 Torr) at 290 °C, though with a partial decomposition.[96]

Evidently, ethoxyiododimethylsilane is formed as an intermediate in the reaction of iodine with allylethoxydimethylsilane, and allyl iodide, ethyl iodide, and permethyloligocyclosiloxanes are the final products.[100] The process occurs according to Eq. (31).

$$\begin{gathered}Me_2(CH_2{=}CH{-}CH_2)SiOEt + I_2 \longrightarrow \\ \longrightarrow Me_2(ICH_2{-}CHI{-}CH_2)SiOEt \xrightarrow[-ICH_2{-}CH{=}CH_2]{\beta\text{-elimination}} \\ \longrightarrow Me_2Si(OEt)I \xrightarrow[-EtI]{} Me_2Si{=}O \longrightarrow 1/n\,(Me_2SiO)_n \qquad (31)\end{gathered}$$

Compounds $R(CH_2{=}CH{-}CH_2)Si(OEt)_2$ (R = Me, Ph) react similarly with iodine. Ethoxyiododimethylsilane is assumed[100] to be an intermediate product of reaction (31). However, its decomposition was interpreted in terms of concepts developed in 1950s (Eq. (32)).

$$\begin{gathered}Me_2Si(OEt)I \longrightarrow [Me_2Si^+OEt]I^- \rightleftharpoons [Me_2Si{=}O^+Et]I^- \longrightarrow \\ \xrightarrow[-EtI]{} [Me_2Si^+{-}O^-] \longrightarrow \text{Polymer} \qquad (32)\end{gathered}$$

Only ethyl iodide is formed in the reaction of iodine with triethoxymethallylsilane. Evidently, the reaction occurs according to the scheme:

$$\begin{gathered}CH_2{=}CMeSi(OEt)_3 + I_2 \longrightarrow ICH_2{-}ICMeSi(OEt)_3 \longrightarrow \\ \xrightarrow[-CH_2{=}CIMe]{\beta\text{-elimination}} ISi(OEt)_3 \longrightarrow (EtO)_2Si{=}O + EtI. \qquad (33)\end{gathered}$$

It is difficult to isolate alkoxyiodosilanes in the free state because of their geminal decomposition even at normal temperature.

An elegant method for reduction of α-arylalkanols by diiododimethylsilane has been developed.[101] However, the author of Ref. 101 could not elucidate the mechanism of the reaction. Presently, this reaction is explained as follows:

$$\begin{gathered}Me_2SiI_2 + HOCRR'Ar \xrightarrow[-HI]{} Me_2Si(OCRR'Ar)I \longrightarrow \\ \xrightarrow[-Me_2Si{=}O]{} ICRR'Ar \xrightarrow{HI} HCRR'Ar + I_2. \qquad (34)\end{gathered}$$

The products of cyclization of the intermediately formed dimethylsilanone $(Me_2SiO)_n$ (*n* = 4, 5) were identified.

The reaction of iodine with 1,3-dicyclohexyldisiloxane also did not result in the corresponding monoiodosubstituted derivatives.[102] Cyclohexyliodosilane $C_6H_{11}SiH_2I$ and oligocyclohexylhydrosiloxanes $(C_6H_{11}SiHO)_n$, probably with $n = 3$ and 4, were the products of this reaction. This is evidence for the geminal decomposition of 1,3-dicyclohexyliodosiloxane $I(C_6H_{11})SiHOSiH_2(C_6H_{11})$ formed as the intermediate. The reaction of disiloxane $H_3SiOSiH_3$ with iodine does not give iodosubstituted disiloxane derivatives. Iodosilane H_3SiI was the only product.[103]

1,3-Dimethyldisiloxane reacts similarly with iodine to form iodomethylsilane $MeSiH_2I$.[104] The reaction of diiodosilane with copper oxide affords not 1,3-diiododisiloxane, but only cyclotetrasiloxane $(H_2SiO)_4$.[60]

We have shown recently* that compounds containing the Si(OM)I group (M = Si, C) do exist and even are donors of silanones. However, they are sufficiently stable only at low temperatures. In particular, they were detected as products of reaction with oxacycloalkanes (oxirane, THF).[12] We have established that the organosilicon compounds containing this fragment, regardless of the route of their formation, decompose easily according to Eq. (3) to generate the corresponding silanone even at room or lower temperature.[6–16]

For example, iodopentamethyldisiloxane decomposes smoothly according to Eq. (35).[7,10–13]

$$IMe_2SiOSiMe_3 \longrightarrow Me_2Si{=}O + ISiMe_3 \qquad (35)$$

Iodotetramethyldisiloxane (Eq. (36)) and 1,3-diiodotetramethyldisiloxane (Eq. (37)) decompose similarly. They are easily formed in the reaction of iodine with 1,1,3,3-tetramethyldisiloxane at 1 : 1 and 2 : 1 molar ratios of the reagents, respectively.

$$\begin{gathered}HMe_2SiOSiMe_2H + I_2 \xrightarrow[-HI]{} \\ \longrightarrow IMe_2SiOSiMe_2H \left\{\begin{array}{l}\xrightarrow[-HI]{} Me_2Si{=}O + Me_2SiHI \\ \xrightarrow{I_2} IMe_2SiOSiMe_2I + HI\end{array}\right. \qquad (36)\end{gathered}$$

$$IMe_2SiOSiMe_2I \longrightarrow Me_2Si{=}O + I_2SiMe_2 \qquad (37)$$

These reactions are a simple and convenient method for the synthesis of iododimethylsilane and diiododimethylsilane. The dimethylsilanone formed as an intermediate is transformed into a mixture of permethylcyclosiloxanes. The thermal decomposition of 1,3-diacetoxy-1,1,3,3-tetramethyldisiloxane resulting in diacetoxydimethylsilane occurs *via* a similar scheme.[5,31]

We have found ingenious routes of formation of dialkylsilanones and alkylhalodisiloxanes for the reac-

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* In cooperation with S. V. Basenko, V. I. Rakhlin, R. G. Mirskov, E. I. Dubinskaya, and I. P. Tsyrendorzhieva.

tions of hexaalkyldisiloxanes with gallium or indium triiodides and tribromides. The reactions proceed according to the general equation (38).[7,10–14]

$$R_3SiOSiR_3 \xrightarrow{MX_3} R_2Si{=}O + SiR_4 \qquad (38)$$

$$R = Alk;\ M = Ga,\ In;\ X = I,\ Br$$

The dialkylsilanones formed were identified as the products of insertion into hexamethyldisiloxane, which is the trapping agent, or the products of their cyclization (peralkyloligocyclosiloxanes). The mechanism of reaction (38) was interpreted by the following scheme:

$$MX_3 + R_3SiOSiR_3 \longrightarrow RMX_2 + XR_2SiOSiR_3, \qquad (39)$$

$$XR_2SiOSiR_3 \longrightarrow R_2Si{=}O + XSiR_3, \qquad (40)$$

$$RMX_2 + XSiR_3 \longrightarrow MX_3 + SiR_4. \qquad (41)$$

Thus, reactions (38)—(41) can be catalytic. GaI_3 is the most active catalyst, and $InBr_3$ is the least active one. We also generated silanones from branched permethyloligosiloxanes $(Me_3SiO)_nSiMe_{4-n}$ (n = 2—4). Their reactivity increases as the number of trimethylsilyloxy groups (n) increases.

The reaction of DMSO with dialkyldichlorosilanes (as well as with $RSiCl_3$ and $SiCl_4$) is another new method for generation of dialkylsilanones.[8] The results obtained were confirmed by American researchers.[33]

The study of the routes of formation and decomposition of organosilicon compounds containing ≡SiOSi and ≡SiOC groups also favored the development of the new concepts considered in this work.

In continuation, an ingenious method for dialkylsilanone generation developed by us can be reported. The method is based on geminal decomposition. This is the reaction of dichlorodiorganylsilanes with salts of several oxygen-containing acids.[16]

$$R_2SiCl_2 + MONO_n \longrightarrow R_2Si{=}O + ClNO_n + MCl \qquad (42)$$

$$M = Na,\ NH_4,\ etc.;\ n = 1,\ 2$$

Thus, one more route for the formation and destruction of the disiloxane SiOSi group resulting in various siloxane structures is the reaction of α-elimination of silanones during the geminal decomposition of monomeric, oligomeric, and polymeric organic and inorganic silicon compounds containing the Si(OR)X group and subsequent processes of their cyclization, polymerization, and insertion into the Si—O bonds of accompanying reagents.

We hope that the data and concepts considered in this review will stimulate further theoretical and synthetic studies in the area of α-elimination of silanones and their subsequent transformations and allow one to develop new technologies in the industry of silicon and related materials.

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