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The third route to the formation of the Si–O–Si-group and siloxane structures. To siloxanes through silanones

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Abstract

On the basis of his own and literature data, the author considers and theoretically substantiates the third route to the formation and decomposition of linear and cyclic oligo- and polysiloxanes, involving intramolecular reactions of geminal fragmentation of $>$Si(OR)X group with the intermediate formation (α-elimination) of short lived silanones $R'_2Si{=}O$. The latter further undergo polymerization or insert into the Si–X bonds (X = O, Cl, etc.) of trapping reagents. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Oligomerization; Polymerization; Oligosiloxanes; Polysiloxanes

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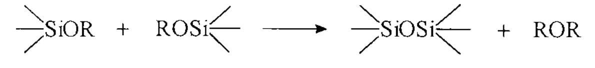
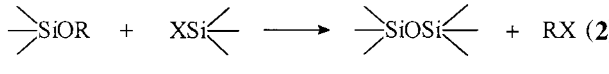
In organic and inorganic chemistry of silicon there is a prevailing idea of two most important pathways to the formation of disiloxane group Si–O–Si which presents the main unit of all the siloxane structures. These (pathways) are intermolecular reactions of homo- and heterocondensation of the corresponding organosilicon monomers and oligomers [1–11] illustrated by Schemes (**1**) and (**2**), respectively:



$$>SiOR + ROSi< \longrightarrow >SiOSi< + ROR$$

(**1**)

R = H [1–14]; Alk [1,2,6,11,15–18]; Ac [11,19–21]; $SiMe_3$ [22,23]; NO_2 [24–26]

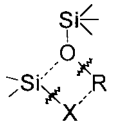


$$>SiOR + XSi< \longrightarrow >SiOSi< + RX$$

(**2**)*

[1]R = H, X = Cl [3,13,27–32], R′O [1–8,11,33], CH_3COO [8,11], R_2N [8,34–36], H [8,37]; R = Alk, X = Cl [1–8,11,38–49], Br [50,51], I [52–54], CH_3COO [1,2,4,6,8,11,45,47], R'_3SiO [1,2,55]; R = $COCH_3$, X = Cl [1,2,6,8,11,44,47]; R = SiR'_3, X = F [1,2,56], Cl, Br, I [57–59]; R = Li, Na, K, X = Cl [47,60–66].

Reactions (**1**) and (**2**) follow a common mechanism. They start with nucleophilic attack of an atom of a Si–O bond-containing reagent on the silicon atom of the second partner, with the formation of intermediate with a pentacoordinate silicon atom and further of a four-membered transion state in which the electron transfer leads to cleavage, thus forming the Si–O–Si group:



In this case a version with X = OR corresponds to reaction (**1**).

It is remarkable that in heterofunctional condensation (**2**) with X = Cl, Br,I; R = hydrocarbon radical (hydrocarbyl) the transition from R = CH_3, CH_2CH_3, $CH(CH_3)_2$ to substituents such as $C(CH_3)_3$ and $CH_2C_6H_5$ able to stabilize the carbocation considerably accelerates the reaction (cf. [48,67–69]). At the same time reaction (**2**) is unrealizable with X = F.

Our researches of low-energy reactions involving the intermediate formation of silanones [70–85], Cherny-

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[1] The great number of examples of reaction (**2**) is caused by not only the absence of reviews devoted to this reaction solely (with the exception of scarce information in the out-of-date book by Sokolov [6]) and by the necessity to compare the inter- and intramolecular pathways to the formation of Si–O–Si group, but also by author's wish to reflect the outstanding contribution made by K.A. Andrianov's school [3–5,12,13,19,27,29,43–47] to the study of heterofunctional condensation leading to the formation of definite siloxane structures.

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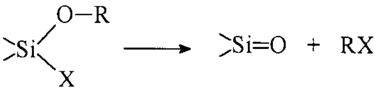
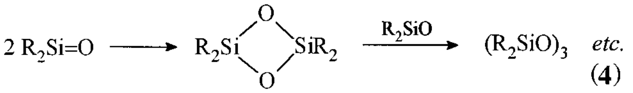
shev's and Krasnova's works devoted to high temperature generation of silanones [86–97] and analysis of the extensive literature show that the processes analogous to reactions (**1**) and (**2**), can proceed intramolecularly in the presence of two geminal reactive substituents OR and X (X = OR is also possible) at the silicon atom, which involves generation of the corresponding silanone according to general scheme (**3**):



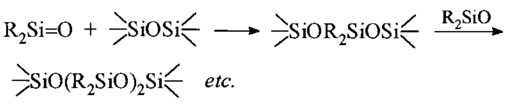
(**3**)

where substituents R and X can be the same as in Eqs. (1) and (2). It is possible to give a set of geminal substituents in group > Si(OR)X which yield silanones according to Scheme (**3**): R = H, X = Cl, OH [12]; R = hydrocarbyl, X = I, Br [77,79–82,98], Cl [40,86–90,94–97], OR′ [15,93]; R = $SiMe_3$, $SiMe_2H$, X = I,Br [70–73,76–82], Cl [92]; R = $SiMe_2X$ (X = I, Br), X = I,Br [70,73,77–82], Cl [99], F [100]; R = COR′, X = $OC(CH_3)_3$ [101,102], OCOR′ [19,20,103]; R = NO_2, X = Cl [104,105]; R = $SiMe_3$, $SiCl_3$, X = Me [92]; R = $S^+Me_2Cl^-$, X = Cl [74,76,77,81,106]; R = M^nX_{n-1} (M = Cu,Hg,Pb,Fe et al.), X = Cl,Br [38,63–66,77,107–111]; R = H, X = hydrocarbyl [112,113]; R = $Sb(OSiMe_3)_2$, X = CH_3 [114]; R = H [1,2], MgBr [115–117], X = $OSiR'_2O^-$.

In organic chemistry such a fragmentation of geminal systems (gem-diols, α-halohydrines, α-haloethers, hemiacetals, etc.) $>C(OR)X \rightarrow >C{=}O + RX$ are so trivial that there is no need citing here the corresponding references. The silanone formed by these reactions, such as dialkylsilanone $R_2Si{=}O$, for example, either undergoes cyclization to the corresponding oligocyclosiloxane according to Scheme (**4**) or inserts into a molecule of a reagent used as a trap or of a certain solvent according to Eqs. 5 and 6. Tetraorganylcyclodisiloxanes $(R_2SiO)_2$ initially formed in the cyclooligomerization of diorganylsilanones were identified by mass spectroscopy (R = C_2H_5) [74] or as the product of insertion into the molecule of 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane (R = C_6H_5) [106]. However, usually tetraorganylcyclodisiloxanes are extremely unstable [106] and readily trap the diorganylsilanone to form hexaorganylcyclotrisiloxane $(R_2SiO)_3$, the primary stable product of diorganylsilanone cyclization.



(**4**)



(**5**)

$$R_2Si{=}O + X{-}M \longrightarrow XR_2SiOM$$

XM = OC, OSi, ClSi, HSi,, OGe, ClGe, OH, ClH [97,118-122].

(**6**)

XM = OC, OSi, ClSi, HSi, OGe, ClGe, OH, ClH [97,118–122].

Reactions (**4**) and (**5**) as a whole are considered as the third route to the formation of diverse siloxane structures basing on silanones. It is the generation and subsequent insertion of silanones into Si–O–Si units of the corresponding monomers, oligomers and polymers according to Schemes (**4–5**) that should be considered as one more mechanism of the formation of polymeric structures together with polyaddition and polycondensation. The surprising thing is that nearly all organosilicon chemists, including those dealing with the chemistry of silanones [86–97,118–124] have given no attention to the possibility and mechanism of geminal fragmentation of the >Si(OR)X group. True enough, in 1917–1919 Stock and Somiesky [107] and in 1952 Andrianov and Sokolov [12] reported a possible intramolecular dehydration (homofunctional geminal fragmentation) 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):

$$R_2Si(OH)_2 \underset{-H_2O}{\rightarrow} R_2Si{=}O \rightarrow 1/n(R_2SiO)_n \qquad (7)$$

R = H [107], Alkyl [12]

$$R_2Si{=}O + HOR_2SiOSiR_2OH$$

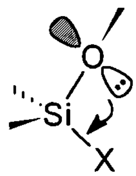
$$\rightarrow HOR_2SiOSiR_2OSiR_2OH \qquad (\mathbf{8})$$

However, the idea prevailing in the middle of the century that existence of the double bond at the silicon atom is impossible made the Russian chemists forget and never remember again their experimental data and the hypothesis proposed. Now nothing else is left but to feel sorry for it. In 1939–1942 possible existence of dialkoxysilanones $(RO)_2Si{=}O$ [15,125] was reported. However these data need a supplementary experimental support.

Let us consider stereoelectronic factors responsible for geminal fragmentation of Si(OR)X group-containing silicon compounds with α-elimination of silanones. This process is also favored by the so called anomeric effect, or α-effect [126–130] known also as n,σ*-conjugation or negative hyperconjugation [131–134]. These effects, though differently called, but the same in content, is of great importance in the transition state and influences much the geminal fragmentation of >Si(OR)X systems. The effect manifests itself in *gauche* conformers and is caused by delocalization of the n-orbital of the oxygen atom lone electron pair onto the antibonding σ*-orbital of the Si–X bond. This leads to the electron charge transfer onto the atom X and to polarization of the Si–X bond. This type of electron density distribution in the H>Si(OR)X system is proved by ^{35}Cl NQR ^{1}H-NMR and IR spectroscopy [135–137], which indicate the chlorine p,σ-electrons, i.e. Si–Cl bond electrons, to be involved in the above interaction, and charge transfer from the oxygen atom onto the acceptor Si–Cl bond [131,132].

It goes without saying that the n, σ^*-conjugation of the oxygen atom in $R'_2Si(OR)X$ molecules is realized with Si–R′ bonds less polar than Si–X bonds, (even if R′ is a hydrocarbon radical). However, its contribution to the electron density distribution in the molecule is less sufficient but it can affect the direction of geminal fragmentation in some instances.

The n,σ^*-conjugation in the RO–Si–X fragment stabilizes the conformation in which the high occupied molecular orbital (HOMO) of the donating oxygen atom p-lone electron pair (LEP) is anti-periplanar with respect to the electron-withdrawing δ^*(Si–X) orbital.



In this case the X atom must be more electronegative than the silicon atom and less electronegative than the oxygen atom ($X \neq F$) [132,134]. As a result of n, σ^*-hyperconjugation the Si–X bond becomes longer whereas the Si–O bond shortens. This effect also changes the valent angles of the central silicon atom and the attached oxygen atom.

The stabilizing n, σ^*-interaction occurs between the occupied donor n-orbital of the oxygen atom lone electron pair and the acceptor antibonding σ^*-orbital of the Si–X group. If the n-orbital contribution to HOMO dominates, the latter is stabilized due to n,σ^*-interaction (its energy reduces and ionization potential increases). Destabilizing interaction takes place between the occupied n-orbital of oxygen lone electron pair and the occupied bonding σ-orbital of the Si–X bond. As a result of n, σ^*-interaction HOMO destabilizes, i.e. its energy enhances and the ionization potential of the oxygen atom reduces. The considerable effect of n, δ^*-conjugation on the stereoelectronic structure of molecules of type $R'_2Si(OR)X$ is proved by both quantum chemical calculation and experimental studies [132,134].

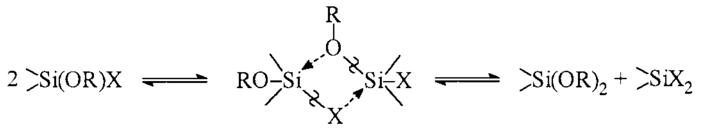
An alternative interpretation of the electron charge distribution in the >Si(OR)X system, that involving an electrostatic directly through field interaction of the oxygen atom charge with the electron cloud of the Si–X bond is also possible [126].

For accomplishing the reaction of α-elimination of silanones it is necessary that the substituent R attached to the oxygen atom in the Si(OR)X group display though weak electrophilic properties. Nucleophilic attack of the atom X on the carbon atom attached to the siloxane oxygen proceeds very easily if the latter is sp^3-hybridized and shows the least electron charge. It should be mentioned that the R–X bond is formed as a result of overlapping of the nucleophile X HOMO with the O–R bond LUMO (the synchronous transition state comes about from mixing the nucleophile X HOMO with the O–R bond LUMO). If R is a hydrocarbon radical, the O–R bond splitting on gem-fragmentation of this group is rather facile when the substituent R structure favors stabilization of the forming carbocation ($R = CMe_3$, $CH_2{-}CH{=}CH_2$, $CH_{3-n}Ph_n$, $n = 1{-}3$ etc.). Thus, for example, α-elimination of dichlorosilanone from benzyloxytrichlorosilane occurs readily at 500–650°C [87].

$$Cl_3SiOCH_2C_6H_5 \xrightarrow{\Delta} Cl_2Si = 0 + ClCH_2C_6H_5 \qquad \textbf{(9)}$$

In contrast to this, methoxytrichlorosilane is stable at as high as 700°C. At this so high temperature Cl_3SiOCH_3 does not form even traces of CH_3Cl and only 5% is disproportionated to give Me_2SiCl_2 and $SiCl_4$ [138].

In this connection it should be emphasized that for organosilicon compounds containing a >Si(OR)X group where R = hydrocarbyl, X = halogen (alkoxyhalosilanes, alkylalkoxyhalosilanes, etc.) gem-fragmentation can follow two directions: (i) intramolecular α-elimination of the corresponding silanone according to reaction (**3**) and (ii) intermolecular reversible disproportionation (equilibrium redistribution of substituents) according to Scheme (**10**) without formation of the SiOSi group [1,2,139].



(10)

Reaction (**10**) involves intermediate transitional four-centered state with pentacoordinate silicon atoms and can be illustrated by a simple example [1,2]:

$$2(RO)SiCl_3 \rightleftharpoons (RO)_2SiCl_2 + SiCl_4 \qquad \textbf{(11)}$$

The alkoxyhalosilanes affinity for disproportionation according to Scheme (**10**) enhances with a decrease of the atomic number and with an increase of the halogen nucleophilicity, whereas that for geminal fragmentation according to Scheme (**3**) shows an inverse order. The disproportionation reaction (**10**) proceeds very readily when X = F (at as low as 20°C). With X = Cl it occurs under more rigid conditions (100–200°C), the rate of alkoxyfluorosilane rearrangement $(RO)_{4-n}SiF_n$ (R =

CH_3, C_2H_5) increases with the number of fluorine atoms in the molecule (n). Compounds of this series with $n = 2$ and 3 easily disproportionate already at nearly room temperature [140–149,162]. Thus, CH_3OSiF_3 disproportionates at $-40°C$ to form mainly $(MeO)_4Si$ and SiF_4 [142].

Alkoxyfluorosilanes and dimethylfluorosilanes are extremely unstable owing to a different electron density distribution in the $>Si(OR)F$ group compared with $>Si(OR)Cl$ (which is indicated, in particular, by the IR spectra of $Me_2Si(OR)X$, $X = F$ and Cl [143] and by enhanced nucleophilicity of the fluorine atom with respect to the silicon atom.

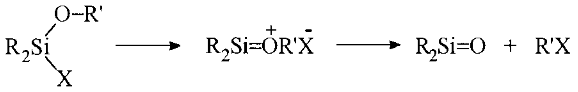
Alkoxy- and phenoxybromosilanes have not been studied much [125,144–147]. No disproportionation has been observed with them. It has been suggested [125] that triethoxybromosilane can disintegrate with elimination of diethoxysilanone:

$$(C_2H_5O)_3SiBr \rightarrow (C_2H_5O)_2Si{=}0 + C_2H_5Br \qquad \textbf{(12)}$$

Alkoxyiodosilanes have not been known till the present time (see below).

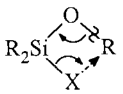
There is also evidence for the possibility of disproportionation of aroxychlorosilanes. In particular, this was demonstrated with dimethylphenoxychlorosilane [148]. However, disproportionation of diphenylphenoxychlorosilane was unsuccessful [149].

The generation of silanones from $R_2Si(OR')X$ molecules is suggested to follow the scheme below:



(13)

However, the formation of a four-centered transition state followed by electron transfer without charge separation (resulting in a decrease in the energy of activation of gem-fragmentation and α-elimination of the corresponding silanone) seems even more possible.



(14)

Compounds having a highly electrophilic substituent R (such as $R = SiF_3H$, for example) or a readily polarizable Si–X bond ($X = I$) are most prone to gem-fragmentation according to the above scheme.

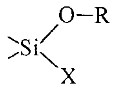
If R in the $>Si(OR)X$ group is a non-activated aromatic substituent such as C_6H_5, for example, no gem-fragmentation is normally observed in these systems. This is conditioned by an increased strength and order of the O–Ar bond and by the fact that the formation of carbocation at the aromatic carbon atom attached to the siloxane oxygen is very hindered owing to the impossibility of stabilizing the carbocation at the expense of internal conjugation (the vacant p-orbital axis is perpendicular to the nucleus π-orbital), the more so that the electron density on the carbon atom is enhanced due to the electron-density transfer from the oxygen atom onto the aromatic ring.

Geminal fragmentation of the Si(OR)X system occurs very easily if the substituent R is a metal ion or metal-containing cation such as MgBr, HgCl, etc. for example. The intermediate products containing geminal fragments of this kind, such as $nSi(OM''X_{n-1})X$, where $M = n-$ valent metal, $X = Cl$, Br, I, are formed during the interaction of H_2SiX_2 or R_2SiX_2 with metal oxides [38,63–66,77,107–111,150], as well as in the reaction of organomagnesium compounds with oligodimethylsiloxane-α,ω-diols or permethylcyclosiloxanes [1,2,113–115].

As early as 1961, basing on X-ray diffraction analysis of silicates we showed first [151,152] the $Si–O^-M^+$ bond in geminal systems $(Si)O–Si–O^-M^+$ to be shorter (1.50–1.60 Å) and the (Si)O–Si bond to be longer (1.70–1.88 Å) than the normal value of Si–O distance (1.64 Å). This points to an increased order (double-bonding) of the Si–OM bond, i.e. 'pre-existence' of the $>Si{=}O$ group and enhanced ionicity of the (Si)O–Si bond, which is in agreement with present ideas on the electron density distribution in $>Si(OR)X$ systems.

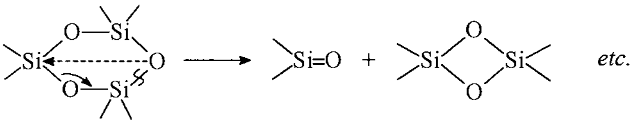
The double-bonding character of the Si–O bond in alkali metal trimethylsilanolates is also implied by its average length of about 1.60 Å [1,2]. In the (Si)O–Si–OM group, along with the increase in the dynamic coefficient and in the Si–OM bond order a decrease in the Si–O–Si bond order (ionicity increase) occurs. In so doing the Si–O–Si angle becomes 8–10° smaller too, which facilitates gem-fragmentation. These conclusions were proved by spectroscopy [153–158]. An increased Si–O bond order in alkali metal trimethylsilanolates was established by ^1H NMR spectroscopy [154]. In the IR spectra of alkali metal trimethylsilanolates [154,155], owing to the increased Si–O bond order the frequencies of antisymmetrical stretching vibrations corresponding to the Si–OM bond dynamic coefficient are enhanced in going from M = Li to M = Cs. In going from M = H to M = Li, Na, K in tetramethyldisiloxanes-1,3-diol and its silanolates $MO(CH_3)_2SiOSi(CH_3)_2OM$ the frequencies of Si–O–Si ν_{as} and ν_s vibrations are diminished [156]. The IR spectrum of sodium trimethylsilanolate and calculation of the frequencies and vibrational modes of its molecule show the SiO^-Na^+ bond to be chiefly ionic [157,158].

The formation of silanones as a result of geminal fragmentation according to Eq. 3 proceeds with great ease, if the silicon atom of the



fragment is bonded to an electronegative atom X possessing a lone electron pair, which is responsible for the nucleophilic nature of the substituent. The above fragmentation is facilitated by an increase in the X atomic radius, the Si–X bond length and polarizability as well as by the associated decrease in the bond energy. This is especially true when $X = I$, since the I^- anion is the most readily leaving group among halogen ions. With $X = F$ the electron density distribution in the RO(F)Si< system is opposite to that with other X groups[2]. Nevertheless, the Si–O bond is shortened (1.56–1.58 Å) in $MeOSiF_3$ and $F_3SiOSiF_3$ seemingly owing to a strong + I-effect of fluorine atoms, whereas the O–R bond polarity is enhanced. Therefore the α-elimination of silanones from geminal systems >Si(OR)F occurs only when the substituent R is a rather powerful electrophile ($R = SiMe_{3-n}F_n$, $n = 1–3$, [100,162–169], BF_2 [100], metal ion, etc.). Gem-fragmentation of this kind is characteristic of the Si–O–Si–F systems since the fluorine atom is the most powerful nucleophile with respect to the silicon atom. We have even found stable Si–F → Si bridges [170].

The thermal destruction of peralkylcyclosiloxanes starts with α-elimination of dialkylsilanone [1,2,118–122,171–175]. This process can be illustrated by the following scheme:



(15)

or, in a more general form,

$$(R_2SiO)_n \xrightarrow[-R_2Si=O]{\Delta} (R_2SiO)_{n-1} \xrightarrow[-R_2Si=O]{} (R_2SiO)_{n-2} \text{ etc.} \qquad \mathbf{(16)}$$

Scheme (**15**) explains why the hexamethylcyclotrisiloxane D_3 is most stable in the thermolysis of permethylcyclosiloxanes D_n [171–175]. At a first glance this seems to be surprising, since the cycle D_3 existing exclusively in a planar strained conformation, turns out to be most reactive of all the permethylcyclosiloxanes (with the only exception of D_2) in heterolytic reactions. This is also in agreement with the lower energy of Si–O bonds in D_3 compared with those in D_4 and D_5 (104.4, 105.9, 106.6 kcal mol^{-1}, respectively) [176–179].

Certain difficulty encountered by geminal fragmentation of peralkylcyclotrisiloxanes according to Scheme (**15**) is caused by conformational rigidity which hinders the formation of the four-centered transition state preceding the α-elimination of disilanone. The tetramethylcyclodisiloxane D_2 formed along with $Me_2Si{=}O$ in D_3 thermolysis is unstable and instantly decomposes to give two molecules of dimethylsilanone. The latter at once inserts either into the D_2 molecule to form D_3 or into the D_3, D_4, D_5 cycles, etc.

$$(Me_2SiO)_3 \underset{+Me_2Si=O}{\overset{-Me_2Si=O}{\rightleftharpoons}} (Me_2SiO)_2 \rightleftharpoons 2(Me_2Si{=}O) \qquad \mathbf{(17)}$$

$$Me_2Si = 0 + (Me_2SiO)_n \rightarrow (Me_2SiO)_{n+1} \qquad \mathbf{(18)}$$

The SiO bond in cyclosiloxanes is exclusively stable to homolytical cleavage [1,2] and their splitting into biradicals $^{\bullet}R_2Si(OSiR_2)_nO^{\bullet}$ is practically unreal.

According to Scheme (**3**) where $R = SiMe_3$, $X = Me$ the destruction of thermally stable hexamethyldisiloxane (conversion ~ 5%) proceeds slowly at 500°C through the intermediate formation of dimethylsilanone to afford linear permethyloligosiloxanes and tetramethylsilane [175]. This process is depicted by Schemes:

$$Me_3SiOSiMe_3 \xrightarrow{500^{\circ}} Me_2Si{=}O + SiMe_4 \qquad \mathbf{(19)}$$

$$Me_3SiOSiMe_3 + nMe_2Si = O \rightarrow Me_3SiO(Me_2SiO)_nSiMe_3, \quad n = 1-3 \qquad \mathbf{(20)}$$

Later the formation of $Me_2Si{=}O$ and $SiMe_4$ by thermolysis of $Me_3SiOSiMe_3$ has been confirmed [92]. HMDS Destruction in plasma proceeds analogously involving the formation of permethyloligosiloxanes and tetramethylsilane although the authors suggest another, less probable scheme of this process [180]. The degree of thermal destruction of low molecular linear permethylsiloxanes $Me_3SiO(Me_2SiO)nSiMe_3$ with $n = 1–6$ increases with the chain length. In this process all their lower homologs down to $n = 0$ [9,181] and permethylcyclosiloxanes $(Me_2SiO)_m$ with $m = 3–6$ are formed. The formation of all the above products of thermolysis can be explained in terms of only the intermediate generation of dimethylsilanone and its further insertion into the Si–O–Si groups and by oligomerization, as was the case with the thermal destruction of permethylcyclosiloxanes [1,2,118–122,171–175]. However, the rate and character of thermal destruction of high molecular permethylpolysiloxanes ($n = 30–100$) are no longer dependent on the macromolecule length [182–188]. This can be explained by a very low content of terminal methyl groups.

The proposed [179] free-radical mechanism of thermal destruction of hexamethyldisiloxane, permethyloligosiloxanes and permethylcyclosiloxanes with homolytic cleavage of the Si–O and Si–C bonds cannot be regarded as correct. However, in 1970 Sobolevsky et al. [175] failed to explain the mechanism of thermal destruction of permethyloligosiloxanes without accepting the possibility of intermediate formation of dimethylsilanone which they dared to modestly denote as biradical $Me_2Si^{\bullet}O^{\bullet}$. Nevertheless, it is, beyond any doubt, a pioneering research, suggested first the intermediate formation of dimethylsilanone (though never

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[2] According to the rule, proposed by us [159,160], in the geminal Y–C–X systems the electron density transition occurs from a more electronegative atom Y onto a less electronegative atom X whereas in the vicinal Y–C–C–X systems the transition is quite the reverse, from X onto Y. This is convincingly supported by ^{35}Cl NQR data [159,160], vibrational and electron spectroscopy data as well as by quantum chemical calculations [161].

called so by the authors). Ultrasound-induced fragmentation of polydimethylsiloxane chains has been assumed [189] to follow a molecular mechanism without formation of macroradicals involving the generation of terminal silanone groups, $-\mathrm{MeSi{=}O}$:

$$\sim \mathrm{Me_2SiO - Me_2SiO - SiMe_2} \sim \;\rightarrow\; \sim \mathrm{MeSi = O} + \mathrm{Me_3Si - O - SiMe_2} \sim \qquad \mathbf{(21)}$$

Thermal destruction (depolymerization) of oligo- and polydialkylsiloxanes containing one or two terminal silafunctional substituents X is of special interest. The destruction of α,ω-functionally substituted polydialkylsiloxanes with the intermediate formation of dialkylsilanone at the expense of gem-fragmentation of terminal $\mathrm{OSiR_2X}$ groups can occur under mild conditions as well. Thus, for example, the reaction of oligodialkylsiloxane-α,ω-diols with organomagnesium compounds of the acetylenic series has been reported to proceed step-by-step involving the intermediate formation of dialkylsilanones [115–117] according to the following scheme:

$$\mathrm{HO(R_2SiO)}_n\mathrm{H} \rightleftharpoons \mathrm{HO(R_2SiO)}_{n-1} + \mathrm{R_2Si{=}O} \qquad \mathbf{(22)}$$

$$\mathrm{R_2Si{=}O} + \mathrm{R'MgX} \rightarrow \mathrm{R_2R'SiOMgX} \overset{\mathrm{H2O}}{\rightarrow} \rightarrow \mathrm{R_2R'SiOH} + \mathrm{HOMgX} \qquad \mathbf{(23)}$$

Further destruction of $\mathrm{HO(R_2SiO)}_{n-1}\mathrm{H}$ follows the same scheme to form finally $(n-1)$ $\mathrm{R_2Si = O}$ further reacting with R′MgX.

The authors noted the difference between terminal and internal Si–O–Si groups in the molecules of oligodialkylsiloxane-α,ω-diols. In their opinion, in the $\mathrm{HO[-R_2SiO-]}_{n-3}\mathrm{-R_2SiO-R_2SiO-R_2SiOH}$ molecule the $\mathrm{Si} \leftarrow$-O-$\rightarrow \mathrm{Si}$ conjugation effect is changed under the influence of the $\mathrm{R_2Si} \leftarrow$-O–H hydroxyl group. This weakens the SiO bond and favors the migration of hydrogen at the Si–O bond splitting site and dialkylsilanone elimination from the molecule. At the same time, the interaction of terminal silanol groups with an organomagnesium reagent to form a geminal SiOMgBr group is quite possible. Such, indeed, should be the case. We can say that Komarov's ideas were rather courageous at that time.

The initial rate of thermal destruction of polydimethylsiloxane-α, ω-diols diminishes with molecular mass, i.e. with decreasing the content of terminal hydroxyl groups. In this case hexamethylcyclotrisiloxane (primary stable product of dimethylsilanone cyclization) is the only product of vacuum thermolysis [1,2]. The depolymerization of these compounds is also favored by thermal destruction of polydimethylsiloxane-α,ω-diols in the presence of water vapors hindering intermolecular anhydrocondensation according to Scheme (**1**).

Gem-fragmentation involving the formation of terminal OSi(=O)Me group can also be responsible for the appearance of negligible quantities of methane during the thermal destruction of permethylsiloxane-α,ω-diols $\mathrm{HO(Me_2SiO)}_n\mathrm{SiMe_2OH}$. The rate of destruction of α,ω-disubstituted polydimethylsiloxanes $\mathrm{X(Me_2SiO)}_n\mathrm{SiMe_2X}$ depends much on the nature of terminal substituents X [1,2,9,188]. This is markedly confirmed by the fact that the replacement of terminal hydroxy groups in polydimethylsiloxane-α,ω-diols by methyl group decreases the rate of thermal destruction of these polymers by a factor of 30–35 [9,184]. Simultaneously, the initial temperature of the destruction process increases from 350–370 to 390–420°C.

In the presence of thermally stable terminal substituents blocking the polydimethylsiloxane macromolecule ($\mathrm{X = CH_3}$, $\mathrm{C_6H_5}$, etc.) the chain rupture with dimethylsilanone elimination can also occur in the internal sites through a four-centered transition state in a way analogous to that mentioned for permethylcyclosiloxanes according to Scheme (**15**). Dimethylsilanone evolved in this case brings about further formation of permethylcyclosiloxanes. Just only this is responsible for the fact that of permethyloligocyclosiloxanes $\mathrm{(Me_2SiO)}_n$ with $n = 3 - 10$ are the products of the thermolysis of linear permethylpolysiloxanes. Their formation due to homolytical rupture of two Si–O bonds at certain sites of the siloxane chain is unlikely. The homolytical stability of the Si–O–Si group is indicated, in particular, by inability of peralkylcyclosiloxanes to undergo free-radically mediated polymerization and their extremely hindered polymerization under the exposure to $^{60}\mathrm{Co}$ γ-irradiation. The radiation-induced polymerization follows an ionic mechanism and its rate is not affected by the presence of diphenylpicrylhydrazyl [1,2]. And, at last, if the thermal destruction of linear and cyclic permethylsiloxanes involved the formation of free radicals, it is the methyl radicals that had to be the primary products of homolytic decomposition, since the Si–C bond energy is considerably lower than the Si–O bond energy (72 and 105 kcal $\mathrm{mol^{-1}}$, respectively). At present it has convincingly been proved that in the depolymerization of polyalkylsiloxanes there is no thermal dissociation of the Si–O bonds very stable to homolytic cleavage [185–188]. Destruction of polydimethylsiloxane chains by intramolecular coordination of silicon and oxygen atoms separated by more than two O–Si groups is rather unlikely because it is very difficult for so remote macromolecular centers to approach each other. All the accumulated experimental data show that the thermal destruction of linear polydialkylsiloxanes starts with the polysiloxane chain ends and proceeds by a mechanism of avalanche-like gem-fragmentation of terminal $\mathrm{Si{-}O{-}SiR_2X}$ groups, which propagates along the chain with elimination of dialkylsilanone further undergoing cyclization (effect of 'falling down dominoes '). This process of polydialkylsiloxane chain destruction involving α-elimination of dialkylsilanones can be presented by the following scheme:

$$\mathrm{X(R_2SiO)}_n\mathrm{SiR_3} \underset{-\mathrm{R_2Si{=}O}}{\rightarrow} \mathrm{X(R_2SiO)}_{n-1}\mathrm{SiR_3} \underset{-\mathrm{R_2Si{=}O}}{\rightarrow} \mathrm{X(R_2SiO)}_{n-2}\mathrm{SiR_3} \qquad \mathbf{(24)}$$

etc. till the final formation of $XSiR_3$ (with $n = 0$).

Depending on the nature of terminal substituents X presenting initial active centers of the depolymerization of α,ω-difunctional polydialkylsiloxanes [185–188], the rate of thermal destruction of $X(R_2SiO)_nSiR_2X$ decreases in the following order of changing X:

$$M(K,Na,Li) > OSO_3H > OH > CH_3 > C_6H_5 \qquad (\mathbf{25})$$

[1,2]

Independently of the nature of ionic catalyst, the ionic and cationic polymerization of peralkylcyclosiloxanes, their depolymerization and reactions of equilibrium distribution occur with ring opening and intermediate formation of an α,ω-difunctional oligomer which contains the same number of silicon atoms and is blocked with ions of the decomposed catalyst at both chain ends:

$$(OSiR_2)_n + X^+Y^- \rightarrow X(OSiR_2)_{n-1}OSiR_2Y \qquad (\mathbf{26})$$

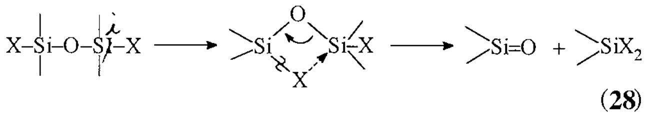
Since α,ω-difunctional oligo- and polydialkylsiloxanes are readily decomposed according to Scheme (**24**) with elimination of highly reactive dialkylsilanones it is suggested that the latter play an essential role in the above mentioned transformations of peralkylcyclosiloxanes. This is completely confirmed by many experimental data summarized in reviews [1,2,9] which cannot be discussed in the present paper.

It should be mentioned that α,ω-difunctional polymers and oligomers are formed in the thermolysis of polyalkylsiloxanes containing an admixture of base and acid polymerization catalysts. Moreover, the catalysts break not only terminal and internal Si–O–Si groups but Si–O bonds as well to form the corresponding silicon-functional substituents X = OH, ONa, OK, OSO_3H etc., [1,2,185].

The mechanism of destruction of α,ω-difunctional oligo- and polydialkylsiloxanes with the intermediate formation of alkylsilanones is conveniently supported by the first members of this homologous series, Si-substituted disiloxanes of general formula X_nR_{3-n}-$SiOSiR_{3-n}X_n$ ($n = 1$–3). Gem-fragmentation of these compounds is illustrated by general equation:

$$X_nR_{3-n}SiOSiR_{3-n}X_n \rightarrow X_{n-1}R_{3-n}Si{=}O + X_{n+1}SiR_{3-n} \qquad (\mathbf{27})$$

Reaction (**27**) seems to occur through the four-centered transition state (**28**). It proceeds very easily with X = F and I. However, the electron density distribution in the transition state is not equal due to a sharp difference in the electronegativity and nucleophilicity of fluorine and iodide atoms. At the same time, an analogous cleavage of compounds with X = Cl and Br is observed only at high temperatures or under the catalytic action of Lewis and Brentsted acids. Coordinating to the siloxane oxygen atom these acids polarize (and weaken) the Si–O bond, thus increasing the Si atom electrophilicity, which facilitates cleavage according to Scheme (**28**):



(**28**)

In accord with the above said, the thermal stability of hexahalodisiloxanes, their near homologs $X_3Si(OSiX_2)_nX$ and cyclic analogs $(X_2SiO)_n$ depends much on the nature of halogen X atom. The lability of fluorosubstituted disiloxanes enhances with the number of fluorine atoms in the molecule.

Thus, hexafluorodisiloxane and octafluorotrisiloxane are very unstable and easily decompose already at room temperature to form SiF_4 and SiO_2 [163,166–169]. Analogously, the gem-fragmentation of ethylpentafluorodisiloxane leads to polyethylsilsesquioxane $(C_2H_5SiO_{1,5})_n$ and SiF_4 at 130°C. 1,3-Diorganyltetrafluorodisiloxanes readily decompose according to general Scheme (**27**) to form the corresponding organyltrifluorosilanes [169].

Under analogous conditions 1,3-dimethyl- and diethyltetrafluorodisiloxanes are converted to the corresponding alkyltrifluorosilanes and a polymer, whereas 1,1,3-triethyltrifluorodisiloxane are transformed to Et_2SiF_2 and 1,3-tetraethyldifluorodisiloxane. The latter can be regarded as the product of $Et_2Si{=}O$ insertion into the Et_2SiF_2 molecule. At the same time, pentaethylfluorodisiloxane is stable at temperatures even exceeding 110°. All the above alkyldifluorodisiloxanes were the reaction products of the corresponding chloroderivatives with NH_4F. Tetramethyl-1,3-difluorodisiloxane slowly but completely decomposes already at room temperature to give $(Me_2SiO)_3$, (the product of trimerization of $Me_2Si{=}O$) and Me_2SiF_2 [100]. The gem-fragmentation of extremely labile 1,3-dimethoxytetrafluorodisiloxane leads to CH_3OSiF_3, $(CH_3O)_2SiF_2$ and polymeric products [169].

Unlike isostructural fluoroderivatives, hexachlorodisiloxane and alkylchlorodisiloxanes are more thermally stable. Only at a temperature of 500–1000° hexachlorodisiloxane and octachlorotrisiloxane decompose according to Scheme (**27**) to afford $SiCl_4$ as well as linear and cyclic perchlorooligosiloxanes [190] with intermediate formation of dichlorosilanone. At even higher temperature (above 1000°C) the thermolysis of these compounds leads to $SiCl_4$ and SiO_2 [191,192].

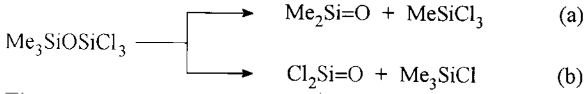
In the presence of tertiary amines the geminal fragmentation of hexachlorodisiloxane slowly proceeds in the same direction already at the boiling point (136°) [190,193,194]. The reaction mechanism proposed by the authors involves an initial stage which is beneath any criticism [193]:

$$R_3N + Cl_3SiOSiCl_3 \rightleftharpoons R_3N^+SiCl_3 + {}^-OSiCl_3 \qquad (\mathbf{29})$$

The catalytic action of tertiary amines on the disproportionation reaction of hexachlorodisiloxanes (and its homologs) is based on the primary formation of their adduct containing a pentacoordinate silicon atom. This gives rise to the electron density transfer onto the oxygen and chlorine atoms which makes further gem-fragmentation much easier

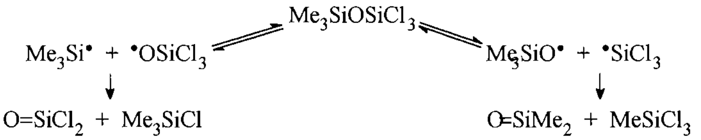
$$R_3N + Cl_3SiOSiCl_3 \rightarrow Cl_3(R_3N)SiOSiCl_3 \rightarrow Cl_2Si{=}O + R_3N + SiCl_4 \qquad \mathbf{(30)}$$

The thermolysis of 1,1,1-trimethyltrichlorodisiloxane proceeds in two directions involving α-elimination of dichlorosilanone and dimethylsilanone.



(31)

These silanones were fixed as the products of insertion into the initial $Me_3SiOSiCl_3$–$Me_3SiOSiCl_2OSiCl_3$ and $Me_3SiOSiMe_2OSiCl_3$, and into $Me_3SiOSiMe_3$ used as a trap, –$Me_3SiOSiCl_2OSiMe_3$ and $Me_3SiOSiMe_2OSiMe_3$, respectively [92]. The reaction mechanism scheme proposed by the authors:



(32)

is unlikely. As mentioned above, the homolytic cleavage of the Si–O bond is rather difficult and the less strong Si–CH_3 bonds should be split first under the conditions studied.

Upon prolonged heating at 175°C 1,3-dichlorotetraalkyldisiloxanes $(ClR_2Si)_2O$ decompose according to Scheme (**27**) to form R_2SiCl_2 and $(R_2SiO)_3$ [99].

Hexabromodisiloxane is considerably less thermally stable than hexachlorodisiloxane. Upon long heating (200–260°) it slowly decomposes to give $SiBr_4$, SiO_2 and a small quantity of $Br(Br_2SiO)_nSiBr_3$, $n = 2-4$. Dodecabromopentasiloxane ($n = 5$) has not been formed a even higher temperatures [166,195–198]. Hexaiododisiloxane $I_3SiOSiI_3$ is unknown and hardly could exist in normal conditions because of decomposition to SiI_4 and SiO_2.

The thermal destruction of hexachlorodisiloxanes to the corresponding tetrahalosilane and silicon dioxide can be demonstrated in the following way:

$$X_3SiOSiX_3 \rightarrow X_2Si = O + SiX_4$$

$$2X_2Si{=}O \rightarrow X_3SiOSi({=}O)X \rightarrow X_4Si + SiO_2;$$

$$X = F, Cl, Br, I \qquad \mathbf{(33)}$$

Our investigations over many years of compounds containing Si–I bonds, in particular, [52–54,70,78,197–213], have shown first their capability for cleavage of C–O–C, C–O–Si and Si–O–Si groups. And not once we tried to synthesize and isolate organic derivatives of silicon-containing I–Si–O–C and I–Si–O–Si groups, such etc. as $ISi(OC_2H_5)_3$, $(CH_3)_2Si(OC_2H_5)I$, $I(CH_3)_2SiOSi(CH_3)_3$, $I(CH_3)_2SiOSi(CH_3)_2I$ for example, but always without success. The existence of I–Si–O–Si containing organosilicon compounds had not been established prior to our investigations. The reactions studied which presumably led to the formation of compounds of this kind formed only the products of gem-fragmentation. All attempts to prepare $>Si(OR)I$-containing alkoxyiodosilanes by the reaction of tetraalkoxysilanes with PI_3 and HI were a failure [125,214]. Alkyliodide and polymers were only the reaction products. The persistent desire to transform alkoxychlorosilanes to the corresponding alkoxyiodosilanes has not been realized either [215]. The reactions of alkoxysilanes $(RO)SiH_3$ ($R = Me$, Et) with iodine and mercury iodide have failed to lead to alkoxyiodosilanes [216]. Nevertheless, the intermediate formation of alkoxyiodosilanes has repeatedly been suggested [125,214,215,217]. And it has been stated that, even unstable, triethoxyiodosilane seems to exist at a temperature below 30° [215]. At the same time, triphenoxyiodosilane proved to be thermally rather stable. It was even possible to distill it in vacuum at 290°, though with partial decomposition [214].

Dimethyliodosilane is likely to be formed as an intermediate in the reaction of iodine with allyldimethylethoxysilane leading to allyliodide, ethyliodide and permethyloligocyclosiloxanes [218]. The process which occurs can be illustrated by the following scheme:

$$Me_2(CH_2{=}CH{-}CH_2)SiOC_2H_5 + I_2 \rightarrow Me_2(ICH_2{-}CH{-}CH_2)SiOC_2H_5 \xrightarrow[-ICH_2-CH=CH_2]{\beta-\text{elimination}} Me_2Si(OC_2H_5)I \xrightarrow[-C_2H_5I]{} Me_2Si{=}O \rightarrow 1/n(Me_2SiO)_n \qquad \mathbf{(34)}$$

The reaction of $R(CH_2{=}CH{-}CH_2)Si(OC_2H_5)_2c$ $R =$ Me, Ph with iodide proceeds in the same way. Dimethyliodoethoxysilane is supposed [218] to be the intermediate of reaction (**34**). However, in the fifties, the decomposition of this compound was interpreted as follows:

$$Me_2Si(OC_2H_5)I \rightarrow [Me_2Si^+OC_2H_5]I^- \rightleftharpoons [Me_2Si\text{——}O^+C_2H_5]I^- \xrightarrow[-C_2H_5I]{} \rightarrow [Me_2Si^+{-}O^-] \rightarrow \text{polymer} \qquad \mathbf{(35)}$$

In the reaction of iodine with methallyltriethoxysilane only ethyodide has been isolated. Evidently, the reaction occurs is as follows:

$$CH_2{=}CMeSi(OC_2H_5)_3 + I_2 \rightarrow ICH_2{-}ICMeSi(OC_2H_5)_3 \xrightarrow[-\,CH_2{=}CIMe]{\beta-\text{elimination}} ISi(OC_2H_5)_5 \rightarrow (C_2H_5O)_2Si{=}O + IC_2H_5 \quad \mathbf{(36)}$$

The difficulty encountered in the isolation of free alkoxyiodosilanes is caused by their geminal fragmentation at already room temperature.

Ando has developed an elegant method for the reduction of α-arylalkanols with dimethyldiiodosilane [219]. However, he has not elucidated the reaction mechanism. At present this process can be presented by the following scheme:

$$Me_2SiI_2 + HOCRR'Ar \xrightarrow[-\,HI]{} Me_2Si(OCRR'Ar)I \xrightarrow[-\,Me_2Si{=}O]{} ICRR'Ar \xrightarrow{+\,HI} HCRR'Ar + I_2 \quad \mathbf{(37)}$$

Cyclization products of the intermediately forming dimethylsilanone $(Me_2SiO)_n$, $n = 4$ and 5 have been identified.

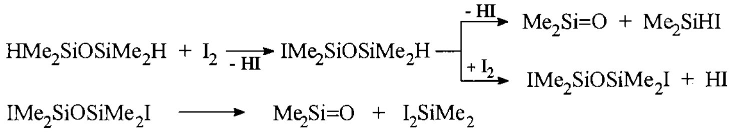
The reaction of iodine with 1,3-dicyclohexyldisiloxane has not formed the corresponding monoiododerivatives either [220]. Cyclohexyliodosilane $C_6H_{11}SiH_2I$ and oligocyclohexylhydrosiloxanes $(C_6H_{11}SiHO)_n$ probably with $n = 3{,}4$ are the products of this reaction. This points to gem-fragmentation of the intermediate 1,3-dicyclohexyliodosiloxane $I(C_6H_{11})SiHOSiH_2(C_6H_{11})$. The reaction of disiloxane $H_3SiOSiH_3$ with iodine does not lead to iododerivatives of disiloxane. The only reaction product was iodosilane H_3SiI [221].

1,3-Dimethyldisiloxane reacts with iodine in an analogous way to form methyliodosilane CH_3SiH_2I [222]. The reaction of diiodosilane with copper oxide gives only cyclotetrasiloxane $(H_2SiO)_4$ rather than 1,3-diiododisiloxane [150].

During the last years together with S.V. Basenko, V.I. Rakhlin, R.G. Mirskov, E.I. Dubinskaya and I.P. Tsyrendorzhieva we have managed to show that compounds containing an >Si(OM)I group where M = Si, C not only exist, but serve as donors for silanones. However, they are rather stable at only low temperatures. In particular, they could be fixed as the products of the reaction with oxacycloalkanes (oxyran, tetrahydrofuran) [79,81]. We have found that organosilicon compounds containing such a fragment are readily decomposed according to Scheme (**3**) to form the corresponding silanone already at room temperature and below [70–85]. Thus, pentamethyliododisiloxane, for example, is easily decomposed according to the scheme [73,76,77,80,81]:

$$IMe_2SiOSiMe_3 \rightarrow Me_2Si = O + ISiMe_3 \quad \mathbf{(38)}$$

Tetramethyliododisiloxane and tetramethyl-1,3-diiododisiloxane smoothly forming in the reaction of iodine with 1,1,3,3-tetramethyldisiloxane in a mole ratio of reagents of 1:1 and 2:1, respectively, are decomposed in a similar manner:



$$HMe_2SiOSiMe_2H + I_2 \xrightarrow[-\,HI]{} IMe_2SiOSiMe_2H \begin{cases} \xrightarrow{-\,HI} Me_2Si{=}O + Me_2SiHI \\ \xrightarrow{+\,I_2} IMe_2SiOSiMe_2I + HI \end{cases} \quad \mathbf{(39)}$$

$$IMe_2SiOSiMe_2I \longrightarrow Me_2Si{=}O + I_2SiMe_2 \quad \mathbf{(40)}$$

These reactions provide a simple and convenient synthetic route to dimethyliodosilane and dimethyldiiodosilane. The intermediate dimethylsilanone is transformed to a mixture of permethylcyclosiloxanes. The thermal destruction of tetramethyl-1,3-diacetoxydisiloxane leading to dimethyldiacetoxy silane follows a similar pathway [11,20].

An original reaction leading to dialkylsilanone and alkylhalodisiloxanes has been found by us in studying the interaction of hexaalkyldisiloxanes with gallium or indium triiodides and tribromides. The reaction occurs according to a general scheme [71,72,76,77,79–82]:

$$R_3SiOSiR_3 \overset{MX_3}{\rightarrow} Me_2Si{=}O + SiR_4$$

$$R = Alk;\ M = Ga, In;\ X = I, Br \quad \mathbf{(41)}$$

The dialkylsilanones formed have been identified either as the products of the insertion into hexamethyldisiloxane serving as a trap, or as the cyclization products, peralkyloligocyclosiloxanes. The mechanism of reaction (**41**) is interpreted in the following way:

$$MX_3 + R_3SiOSiR_3 \rightarrow RMX_2 + XR_2SiOSiR_3 \quad \mathbf{(42)}$$

$$XR_2SiOSiR_3 \rightarrow R_2Si = 0 + XSiR_3 \quad \mathbf{(43)}$$

$$RMX_2 + XSiR_3 \rightarrow MX_3 + SiR_4 \quad \mathbf{(44)}$$

Thus, reactions (**41–44**) can be performed catalytically. In this case GaI_3 is the most powerful catalyst, whereas $InBr_3$ shows the least catalytic activity. The reaction of generation of silanones also was carried out with branching permethyloligosiloxanes $(Me_3SiO)_nSiMe_{4-n}$ ($n = 2$–4). The reactivity of these siloxanes enhances with the number of trimethylsiloxy groups (n).

An alternative new pathway found by us for the generation of dialkylsilanones is provided by the reaction of dimethylsulfoxide with dialkyldichlorosilanes (as well as with $RSiCl_3$ and $SiCl_4$) [74]. It is very nice that our data have been supported by the American colleagues [106].

It is the investigation of new ways of the formation and destruction of organosilicon compounds containing I–Si–O–Si and I–Si–O–C groups that has led us to the new concepts discussed in the present paper. In conclusion, we would like to report a completely new method for the generation of dialkylsilanones, based on gem-fragmentation, namely the reaction of diorganyldichlorosilanes with metal or ammonium salts of many oxygen-containing acids [104,105]. For example,

$$R_2SiCl_2 + MONO_n \rightarrow R_2Si{=}O + ClNO_n + MCl \qquad \textbf{(45)}$$

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

Thus, the third route to the formation of disiloxane Si–O–Si group and diverse siloxane structures involves the reaction of α-elimination of silanones in gem-fragmentation of monomeric, oligomeric and polymeric organic and inorganic compounds of silicon, containing a $>$Si(OR)X group, and further processes of their cyclization, polymerization and insertion into the Si–O bond of the attendant reagents.

I cherish a hope that the data and ideas presented in this paper will lead not only further theoretical and synthetic investigations into the α-elimination of silanones and their subsequent transformations, but will enable new technologies in the production of silicones and silicone-based materials to be developed.

Acknowledgements

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References

[1] M.G. Voronkov, V.P. Mileshkevich, Yu.A. Yuzhelevskii, Siloksanovaya svyaz', Novosibirsk, Nauka, 1976, p. 413 S.

[2] M.G. Voronkov, V.P. Mileshkevich, Yu.A. Yuzhelevskii, The Siloxane Bond, Consultants Bureau, New York–London, 1978, p. 493.

[3] K.A. Andrianov, Khimiya kremneorganicheskikh soedinenii, Moskva, Goskhimizdat, 1955, p. 520 S.

[4] K.A. Andrianov, Polimery s neorganicheskimi glavnymi tsepyami molekul, Moskva, Izd. Akad. Nauk SSSR, 1962, p. 325 S.

[5] K.A. Andrianov, Metody elementoorganicheskoi khimii. Kremnii, Moskva, Nauka, 1968, p.p. S. 548–569, 596–601.

[6] N.N. Sokolov, Medoty sinteza poliorganosiloksanov, M.-L., Gosenergoizdat, 1959, p. 197 S.

[7] C. Eaborn, Organosilicon Compounds, Butterwoths Science, London, 1960, p. 530.

[8] W. Noll, Chemie und Technologic der Silicone, Verlag Chemie, Weinheim, 1968, p. 612 S.

[9] T.C. Kendrick, B. Parbhoo, J.W. White, in: S. Patai, Z. Rapporport (Eds.), The Chemistry of Organosilicon Compounds, Wiley, Cambridge, 1989, pp. 1289–1362.

[10] S.J. Clarson, J.A. Semlyen, Siloxane Polymers, PTR Prentice-Hall, Englewood Glifts, New York, 1993.

[11] M.G. Voronkov, N.G. Sviridova, Usp. Khim. 40 (1971) 1761.

[12] K.A. Andrianov, N.N. Sokolov, Dokl. Akad. Nauk SSSR 82 (1952) 909.

[13] K.A. Andrianov, V.V. Severny, Zh. Org. Khim. 32 (1962) 1633.

[14] A.I. Petrashko, Dokl. Akad. Nauk SSSR 180 (1968) 1116.

[15] A.M. Samsonia, Uchenye zapiski LGU 40 (1939) 51.

[16] Yu.N. Vol'nov, Zh. Obshch. Khim. 17 (1947) 1428.

[17] G.H. Wagner, C.E. Erickson, Pat. USA, (1956) 2731485; Chem Abstr. 50 (1956) 8247.

[18] B.A. Bolotov, N.P. Kharitonov, E.A. Bataev, E.G. Rumyantseva, Zh. Obshch. Khim. 37 (1947) 2113.

[19] K.A. Andrianov, A.A. Zhdanov, S.A. Pavlov, Dokl. Akad. Nauk SSSR 102 (1955) 85.

[20] M.G. Voronkov, N.G. Sviridova, I.B. Klemenko, N.G. Shchikunov, V.A. Churmaeva, Zh. Obshch. Khim. 39 (1969) 2502.

[21] M.G. Voronkov, N.G. Sviridova, Zh. Obshch. Khim. 40 (1970) 90.

[22] M.G. Voronkov, O.S. Stankevich, N.I. Shergina, E.I. Dubinskaya, Zh. Obshch. Khim. 64 (1994) 158.

[23] M.G. Voronkov, O.S. Stankevich, N.I. Shergina, E.I. Dubinskaya, Zh. Obshch. Khim. 64 (1994) 15733.

[24] M.G. Voronkov, E.A. Maletina, V.K. Roman, Zh. Obshch. Khim. 45 (1965) 1900.

[25] M.G. Voronkov, E.A. Maletina, V.K. Roman, Kremnekislorodnye Soedineniya Nemetallov. Proizvodnye Azota i Fosfora, Novosibirsk, Nauka, 1988, p. 365.

[26] M.G. Voronkov, E.A. Maletina, V.K.Roman, Heterosiloxans, Derivatives of Nitrogen and Phosphorus, vol. 2, Harwood Academy, London, 1991, p. 489.

[27] K.A. Andrianov, S.A. Golubtsov, N.N. Sokolov. Vysokomolek. Soed. (1952) 1.

[28] R.H. Leitheiser, Pat. Germ. (1961) 1157611; Pat. USA (1960) 3122579; C.A. 60 (1965) 3076.

[29] A.A. Zhdanov, K.A. Andrianov, P.V. Astapova, G.F. Vinogradova, Izv. Akad. Nauk SSSR Ser. Khim. (1973) 26728.

[30] A.A. Zhdanov, P.V. Astapova, B.D. Lavrukhin, Izv. Akad. Nauk SSSR Ser. Khim. (1985) 657.

[31] N.N. Makarova, B.D. Lavrukhin, G.N. Turkel'taut, N.N. Kuzmin, I.M. Putrova, E.B. Matukhina, Izv. Akad. Nauk SSSR Ser. Khim. (1989) 1351.

[32] N.N. Makarova, T.V. Astapova, B.D. Lavrukhin, Izv. Akad. Nauk SSSR Ser. Khim. (1996) 958.

[33] B. Smith, Svensk. Kem. Tidsk 67 (1955) 421.

[34] B. Smith, Svensk. Kem. Tidsk 65 (1953) 101.

[35] R.E. Burks, E.R. Covington, M.V. Jacksoon, J.E. Curry, J. Polym. Sci. Polym. Chem. Ed. 11 (1973) 319.

[36] P.R. Drovnick, R.W. Lenz, J. Polym. Sci. Polym. Chem. Ed. 20 (1982) 1951.

[37] N.F. Orlov, B.N. Dolgov, Dokl. Akad. Nauk SSSR 125 (1959) 817.

[38] A. Stokes, Am. Chem. J. 14 (1892) 438, 545.

[39] H. Post, J. Org. Chem. 5 (1940) 443.

[40] R.O. Sauer, Pat USA 2 (1950) 534 149; C.A. 45 (1951) 4739.

[41] C.I. Guillissen, A. Gancberg, Chem. Age 66 (1952) 976.

[42] C.J. Guillissen, A. Gancberg, Jnd. Chim. Belge 20 (1955) 382.

[43] K.A. Andrianov, T.N. Ganina, N.N. Sokolov, Zh. Obshch. Khim. 26 (1956) 1691.

[44] K.A. Andrianov, N.N. Sokolov, E.N. Khrustaleva, Zh. Obshch. Khim. 26 (1956) 1102.

[45] N.N. Sokolov, K.A. Andrianov, Izv. Akad. Nauk SSSR Otd. Khim. Nauk, (1957) 806.

[46] K.A. Andrianov, T.N. Ganina, N.N. Sokolov, Zh. Obshch. Khim. 30 (1960) 2777.

[47] K.A. Andrianov, E.A. Burlova, E.S. Tikhonov, Zh. Obshch. Khim. 39 (1969) 1789.

[48] B.J.P. Corriu, D. Leclercq, P.H. Mutin, H. Samson, A. Vioux, J. Organomet. Chem. 466 (1994) 43.

[49] P. Servais, Pat. USA, 2 485 928, C.A., 44 (1950) 3007; Pat. Brit. 655 003 C.A. 46 (1952) 2094.

[50] M. Kumada, J. Inst. Polytech. Osaka City Univ. Ser. C 2 (1952) 147.

[51] K. Moedritzer, J. Van Wazer, Makromol. Chem. 104 (1967) 148.

[52] M.G. Voronkov, Yu.I. Khudobin, Zh. Obshch. Khim. 26 (1956) 2584.

[53] M.G. Voronkov, S.F. Pavlov, E.I. Dubinskaya, Izv. Akad. Nauk SSSR Ser. Khim. (1975) 657.

[54] M.G. Voronkov, S.F. Pavlov, E.I. Dubinskaya, Dokl. Akad. Nauk SSSR 227 (1976) 67.

[55] M.G. Voronkov, Zh. Obshch. Khim. 9 (1959) 907.

[56] M.G. Voronkov, S.V. Basenko, I.A. Gebel, V.Yu. Vitkovskii, R.G. Mirskov, J. Organomet. Chem. 433 (1992) 1.

[57] M.G. Voronkov, L.M. Chudesova, Zh. Obshch. Khim. 29 (1959) 1534.

[58] M.G. Voronkov, S.F. Pavlov, E.I. Dubinskaya, Dokl. Akad. Nauk SSSR 227 (1986) 362.

[59] M.G. Voronkov, S.V. Basenko, Heterolytic Cleavage Reactions of Siloxane Bond. Soviet scientific reviews, Section B., vol. 15, part 1, Harwood Academic, London, 1990, p. 1.

[60] K. Rühlmann, U. Scheim, K. Käppler, R. Gewald, in: A.R. Bassindale, P.P. Gaspar (Eds.), Frontiers of Organosilicon Chemistry, The Royal Society of Chemistry, London, 1991, p. 208.

[61] L.H. Sommer, L.A. Green, F.C. Whitmore, J. Am. Chem. Soc. 71 (1949) 3253.

[62] J.F. Hyde, O.K. Johannson, W.H. Daudt, R.F. Fleming, H.B. Laudenslager, M.P. Roche, J. Am. Chem. Soc. 75 (1953) 5615.

[63] S.N. Borisov, M.G. Voronkov, E.Ya. Lukevits, Kremneelementoorganicheskie soedineniya, Khimiya, Leningrad, 1966, 541 S.

[64] S.N. Borisov, M.G. Voronkov, E.Ya. Lukevits, Organosilicon heteropolymers and heterocompounds, Plenum Press, New York, 1970, p. 632.

[65] M.G. Voronkov, E.A. Maletina, V.K. Roman, Geterosiloksany, Novosibirsk, Nauka, 1984, 265 S.

[66] M.G. Voronkov, E.A. Maletina, V.K. Roman, Heterosiloxanes, Derivatives of Non-Biogenic Elements, vol. 1, Harwood Academy, London, 1988, p. 469.

[67] R.J.P. Corriu, D. Leclercqs, P. Lefevre, P.H. Mutin, A. Vioux, J. Non-Cryst. Solids 146 (1992) 301.

[68] R.J.P. Corriu, D. Leclercqs, P. Lefevre, P.H. Mutin, A. Vioux, J. Mater. Chem. 2 (1992) 673.

[69] R.J.P. Corriu, D. Leclercqs, P. Lefevre, P.H. Mutin, A. Vioux, Chem. Mater 4 (1992) 961.

[70] M.G. Voronkov, Yu.A. Turkin, R.G. Mirskov, E.E. Kuzmina, V.I. Rakhlin, Zh. Obshch. Khim. 59 (1989) 611.

[71] M.G. Voronkov, S.V. Basenko, M.V. Ustinov, Zh. Obshch. Khim. 63 (1993) 2155.

[72] M.G. Voronkov, S.V. Basenko, M.V. Ustinov, Dokl. Akad. Nauk 333 (1993) 180.

[73] S.V. Basenko, M.G. Voronkov, Dokl. Akad. Nauk 339 (1994) 204.

[74] S.V. Basenko, M.G. Voronkov, Dokl. Akad. Nauk 339 (1994) 486.

[75] S.V. Basenko, M.G. Voronkov, R.G. Mirskov, Inventor's Certificate 2058318, 1994.

[76] M.G. Voronkov, S.V. Basenko, M.V. Ustinov, Zh. Onshch. Khim. 65 (1995) 1482.

[77] M.G. Voronkov, S.V. Basenko, J. Organomet. Chem. 500 (1995) 325.

[78] Yu.A. Turkin, P.V. Arbuzov, R.G. Mirskov, M.G. Voronkov, V.I. Rakhlin, Tezisy Dokl, IV Vsesoyuzn. konf. Stroenie ireaktsionnaya sposobnost' kremneorg. soed, Irkutsk, 1993 S. 64, 175.

[79] M.G. Voronkov, S.V. Basenko, M.V. Ustinov, 21th Symp. Heteroatom. Chemistry, Toyama, Abstr. 1993, p. 117.

[80] M.G. Voronkov, S.V. Basenko. Tezisy dokl. Andrianovskie chteniya, Moskva, 1995, S. 4.

[81] M.G. Voronkov, 28th Organosilicon Symposium, Gainsville USA, 1995, A 21.

[82] M.G. Voronkov, S.V. Basenko. Tezisy dokl. V Vseross. simp. Strooenie i reaktsionnaya sposobnost' kremneorg. soed, Irkutsk, 1996, S. 45, 78, 79.

[83] M.G. Voronkov, S.V. Basenko, I.A. Gebel, R.G. Mirskov, XIth International Symp. Organosilicon Chemistry, Montpellier, France, 1996, p. 32.

[84] E.I. Dubinskaya, I.P. Tsyrendorzhieva, M.G. Voronkov, XIth International Symp. Organosilicon Chemistry, Montpellier, France, 1996, PC 67, PC 68, PC 69.

[85] E.I. Dubinskaya, I.P. Tsyrendorzhieva, M.G. Voronkov, Tezisy dokl. V Vseross.simp. Stroenie i reaktsionnaya sposobnost' kremneorg.soed., Irkutsk, 1996, S. 43, 44, 47, 97.

[86] A.V. Golovkin, N.A. Mudrova, T.L. Krasnova, L.V. Serebrennikova, V.S. Nikitin, E.A. Chernyshov, Zh. Obshch. Khim. 55 (1985) 2802.

[87] E.A. Chernyshov, T.L. Krasnova, N.A. Mudrova, A.V. Golovkin, M.G. Kuznetsova, Zh. Obshch. Khim. 57 (1987) 1725.

[88] E.A. Chernyshov, T.L. Krasnova, N.A. Mudrova, A.B. Petrunin, G.N. Turkeltaub, Zh. Obshch. Khim. 60 (1990) 1078.

[89] E.A. Chernyshov, N.A. Mudrova, T.L. Krasnova, M.G. Kuznetsova, G.N. Turkeltaub, Zh. Obshch. Khim. 60 (1990) 1674.

[90] E.A. Chernyshov, N.A. Mudrova, T.L. Krasnova, A.B. Petrunin, G.N. Turkeltaub, Zh. Obshch. Khim. 61 (1991) 916.

[91] E.A. Chernyshov, N.A. Mudrova, T.L. Krasnova, Yu.M. Ushakov, A.B. Petrunin, M.G. Kuznetsova, Zh. Obshch. Khim. 62 (1992) 1308.

[92] T.L. Krasnova, E.A. Chernyshov, A.P. Sergeev, Izv. Akad. Nauk Ser. Khim. (1996) 1299.

[93] E.A. Chernyshov, T.L. Krasnova, A.P. Sergeev, Izv. Akad. Nauk Ser. Khim. (1996) 1577.

[94] E.A. Chernyshov, T.L. Krasnova, N.A. Mudrova, Tezisy Dokl, IV Vsesoyuzn.konf. Stroenie i reaktsionnaya sposobnost' kremneorg.soed, Irkutsk (1993) S. 133.

[95] E.A. Chernyshev, Xth International Symposium on Organosilicon Chemistry, Abstracts, Poznan (Poland), 1993, p. 38.

[96] E.A. Chernyshov, T.L. Krasnova, Tezisy I kremneorg. mikrosimp., Moskva—N.Novgorod, 1994, S.12,13.

[97] E.A. Chernyshov, T.L. Krasnova, Tezisy dokl. Andrianovskie hteniya, Moskva, 1995, S.15.

[98] M. Kumada, H. Hattori, J. Inst. Polytech., Osaka City Univ. Ser. C, V. 3, P. 77.

[99] P.A. McCusker, T. Ostdick, J. Am. Chem. Soc. 80 (1958) 1103.

[100] P.A. McCusker, T. Ostdick, J. Am. Chem. Soc. 81 (1959) 5550.

[101] M.G. Voronkov, V.P. Davydova, A.N. Lazarev, Zh. Obshch. Khim. 28 (1958) 2128.

[102] S.V. Basenko, M.G. Voronkov, Tezisy dokl. V Vseross.simp. Stroenie i reaktsionnaya sposobnost' kremneorg.soed, Irkutsk, 1996, S. 79.

[103] S.V. Basenko, P.A. Bormashev, R.G. Mirskov, M.G. Voronkov, Dokl. Akad. Nauk SSSR 33 (1990) 177.

[104] E.I. Dubinskaya, I.P. Tsyrendorzhieva, A.I. Albanov, M.G. Voronkov, XIth International Symposium on Organosilion Chemistry, Abstracts, Montpellier, France, 1996, PC 67.

[105] E.I. Dubinskaya, I.P. Tsyrendorzhieva, A.I. Albanov, G.Yu. Tikhii, M.G. Voronkov, Tezisy dokl. V Vseross.simp. Stroenie i reaktsionnaya sposobnost' kremneorg.soed, Irkutsk, 1996, S.43.

[106] Ping Lu, J.K. Paulasari, W.P. Weber, Organometallics, 15 (1996) 4649.

[107] A. Stock, C. Somieski, Chem. Ber. 50 (1919) 1764; 52 (1919) 1851.

[108] L.R. Vyle, F.S. Kipping, J. Chem. Soc. London 125 (1924) 2616.

[109] T. Takiguchi, M. Sakurai, T. Kishi, J. Ichimura, I. Jizuka, J. Org. Chem. 25 (1960) 310.

[110] J.F. Hyde (Dow Corning Corp.) Pat. USA 2 629 725, 1953; C.A. 47 (1953) 5720e.

[111] J.F. Hyde (Dow Corning Corp.) Pat. USA (1953) 2 629 726; C.A. 47 (1953) 5720g.

[112] Z.H. Aiube, J. Chojnouski, C. Eaborn, W.A. Stanczyk, J. Chem. Soc. Chem. Commun. (1983) 493.

[113] C. Eaborn, W.A. Stanczyk, J. Chem. Soc. Perkin Trans (II) (1984) 2099.

[114] M.G. Voronkov, S.V. Basenko, V.Yu. Vitkovskii, S.M. Nozdrya, R.G. Mirskov, Metalloorg. Khimiya 2 (1989) 310.

[115] N.V. Komarov, Yu.V. Maroshin, A.D. Lebedeva, L.N. Astafieva, Izv. Akad. Nauk SSSR (1963) 92.

[116] M.F. Shostakovsky, N.V. Komarov, Yu.V. Maroshin, Zh. Obshch. Khim. 35 (1965) 335.

[117] M.F. Schostakovsky, N.V. Komarov, J. Prakt. Chem. 23 (1964) 208.

[118] L.E. Gusel'nikov, N.S. Nametkin, V.M. Vdovin, Usp. Khim. 52 (1974) 1317.

[119] L.E. Gusel'nikov, N.S. Nametkin, V.M. Vdovin, Accounts Chem. Res. 8 (1975) 18.

[120] L.E. Gusel'nikov, N.S. Nametkin, Chem. Rev. 79 (1979) 529.

[121] G. Raabe, J. Michl, Chem. Rev. 85 (1985) 419.

[122] G. Raabe, J. Michl, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Organic Silicon Compounds, Wiley Chichester, London, UK, Chapter 17, 1989, p. 1013.

[123] V.N. Khabashesku, Z.A. Kerzina, A.K. Maltsev, O.M. Nefedov, J. Organomet. Chem. 364 (1989) 301.

[124] A.K. Maltsev, V.N. Khabashesku, O.N. Nefedov, in: E.R. Corey, J.Y. Corey, P.P. Gaspar (Eds.), Silicon Chemistry, Wiley, New York, 1987, pp. 211–224.

[125] H.N. Post, H.M. Norton, J. Org. Chem. 7 (1942) 528.

[126] V.P. Feshin, L.S. Romanenko, M.G. Voronkov, Usp. Khim. 50 (1981) 461.

[127] N.S. Zefirov, N.M. Shektman, Usp. Khim. 40 (1971) 494.

[128] P. Deslongchamps, Stereoelectronic Effects in Organic Chemistry, Pergamon Press, Oxford, 1983.

[129] J. Tvaroska, T. Bleha, Chem. Pap. 39 (1985) 805.

[130] A.J. Kirby, The Anomeric Effect and Related Stereoelectronic Effects at Oxygen, M., Mir, 1985, p. 171.

[131] Y. Apeloig, A. Stanger, J. Organomet. Chem. 346 (1988) 305.

[132] Y. Apeloig, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Organic Silicon Compounds, Wiley, New York, 1989, p. 59.

[133] A.E. Reed, P.R. Schleyer, Inorg. Chem. 27 (1988) 3969.

[134] R.P. Arshinova, Metallorg. Khim. 3 (1990) 1127.

[135] I.P. Biryukov, M.G. Voronkov, E. Ya. Lukevits, I.A. Safin, Teoret. i Eksperim Khim. 6 (1970) 566.

[136] V.P. Feshin, M.G. Voronkov, G. Ya Zueva, L.S. Romanenko, G.V. Lipatova, Dokl Akad. Nauk SSSR 232 (1977) 1370.

[137] A.N. Egorochkin, S.Ya. Khoroshev, N.S. Vyazankin, T.I. Chernysheva, O.V. Kuzmin, Izv. Akad. Nauk SSSR Ser. Khim. (1971) 544.

[138] J. Goubau, H. Behz, J. Anorg. Allg. Chem. 272 (1953) 2.

[139] J.R. Van Waser, K. Moedritzer, J. Inorg. Nucl. Chem. 26 (1964) 737.

[140] D.E. Peppard, W.U. Brown, W.C. Jonson, J. Am. Chem. Soc. 68 (1946) 76.

[141] W. Alrey, G.M. Shedrick, J. Inorg. Nucl. Chem. 32 (1970) 1827.

[142] V.G. Noskov, L.N. Kalinina, M.A. Englin, Zh. Obshch. Khim. 42 (1972) 2028.

[143] P. Koehler, H. Weydig, K. Licht, Z. Chem. 3 (1977) 100.

[144] A. Radecki, R. Piekoš, Roczn. Chem. 36 (1962) 177.

[145] A. Radecki, Roczn. Chem. 37 (1963) 727.

[146] A. Radecki, R. Piekoš, Roczn. Chem. 35 (1961) 869.

[147] A. Radecki, R. Piekoš, Roczn. Chem. 36 (1962) 1329.

[148] Yu.M. Varezhkin, D. Ya Zhinkin, M.M. Morgunov, V.P. Ansov, Zh. Obshch. Khim. 47 (1977) 2089.

[149] A.N. Mikhailova, M.M. Morgunova, D.Ya. Zhinkin, G.L. Merkulova, Zh. Obshch. Khim. 47 (1977) 2087.

[150] C. Glidewell, A.G. Robiette, G.M. Sheldrick, J. Chem. Soc. Chem. Commun., 1970, p. 931.

[151] M.G. Voronkov, Dokl. Akad. Nauk SSSR 138 (1961) 106.

[152] M.G. Voronkov, Zh. Obshch. Khim. 32 (1962) 2391.

[153] A.N. Lazarev, Izv. Akad. Nauk SSSR, Ser. Khim. (1964) 235.

[154] H. Schmidbaur, J.A. Perez-Garsia, H.S. Arnold, Z. Anorg. Chem. 328 (1964) 105.

[155] W.S. Taflock, E.G. Rochow, J. Org. Chem. 17 (1952) 1555.

[156] A.N. Lazarev, G.F. Tenisheva, V.P. Davydova, Dokl. Akad. Nauk SSSR 158 (1964) 648.

[157] A.N. Lazarev, K. Poiker, G.F. Tenisheva, Dokl. Akad. Nauk SSSR 175 (1967) 1322.

[158] K. Poiker, A.N. Lazarev, Izv. Akad. Nauk SSSR, Neorganich. Materialy 4 (1968) 1716.

[159] M.G. Voronkov, G.V. Dolgushin, V.P. Feshin, L.P. Turchaninova, N.A. Korchevin, E.N. Deryagina, Zh. Obshch. Khim. 62 (1992) 1111.

[160] M.G. Voronkov, G.V. Dolgushin, V.P. Feshin, L.P. Turchaninova, N.A. Korchevin, E.N. Deryagina, Z. Naturforsch. 47A (1992) 147.

[161] E.I. Brodskaya, G.V. Rotovsky, G.A. Yuzhakov, V.V. Belyaeva, M.G. Voronkov, Zh. Obshch. Khim. 67 (1997), in press.

[162] H.J. Emeleus, H.G. Heal, J. Chem. Soc. (1949) 1696.

[163] D.C. Payne, J. Chem. Soc. (1954) 2143.

[164] B.J. Aylett, I.A. Ellis, J.R. Richmond, J. Chem. Soc. Dalton Trans. 9 (1973) 981.

[165] J. Goubeau, H. Grosse-Ruyken, Z. Anorg. Chem. (1951) 230.

[166] H.S. Booth, R.S. Osten, J. Am. Chem. Soc. 67 (1945) 1092.

[167] M. Chaignear, Compt. Rend. 266 (1968) 1053.

[168] K.G. Sharp, J.L. MacGrave, J. Inorg. Nucl. Chem. 33 (1971) 2813.

[169] T. Margrave, K.G. Sharp, P.W. Wilson, J. Am. Chem. Soc. 92 (1970) 1530.

[170] Yu.L. Frolov, T.N. Aksamentova, G.A. Gavrilova, N.N. Chipanina, V.B. Modonov, L.I. Gubanova, V.M. D'yakov, M.G. Voronkov, Dokl. Akad. Nauk SSSR 267 (1982) 646.

[171] T.Kh. Islamov, Candidate Dissertation, M., 1970.

[172] L.E. Gusel'nikov, T.Kh. Islamov, V.M. Vdovina, N.S. Nametkin, Tezisy dokl. Soveshchaniya Vliyanie vysshikh atomnykh orbitalei na fizich. i khimich. svoistva elementov, Zinatne Publishers, Riga, 1971, S. 74.

[173] L.E. Gusel'nikov, N.S. Nametkin, T.Kh. Islamov, A.A. Sobtsov, V.M. Vdovin, Izv. Akad. Nauk SSSR Ser. Khim. (1971) 84.

[174] I.M.T. Davidson, J. Thompson. J. Chem. Soc. Chem. Commun. (1971) 251.

[175] M.V. Sobolevsky, I.I. Skorokhodov, V.E. Ditsent, L.V. Sobolevskaya, G.M. Moiseeva, Vysokomolek. Soed. 12A (1970) 2714; 16A (1974) 729.

[176] M.G. Voronkov, Zh. Obshch. Khim. 66 (1996) 167.

[177] M.G. Voronkov, V.A. Klyuchnikov, L.I. Marenkova, Dokl. Akad. Nauk 344 (1995) 489.

[178] M.G. Voronkov, V.A. Klyuchnikov, E.V. Mironenko, G.N. Shvets, T.F. Danilova, Yu.I. Khudobin, J. Organomet. Chem. 406 (1991) 91.

[179] M.G. Voronkov, V.A. Klyuchnikov, L.I. Marenkova, J. Organomet. Chem. 510 (1996) 263.

[180] M.R. Alexander, R.D. Short, F.R. Jones, XI ith Intern. Symp. on Organosilicon Chemistry, Montpellier (France) 1996, OC 19.

[181] T.H. Thomas, T.C. Kendrick, J. Polym. Sci. Part. A-2 7 (1969) 537.

[182] M.V. Sobolevsky, I.I. Skorokhodov, V.E. Ditsent, L.V. Sobolevskaya, G.M. Moiseeva, Vysokomolek. Soed. 15 (1973) 507.

[183] Yu.A. Aleksandrov, T.C. Nikitina, A.N. Pravednikov, Vysokomolek..soed. X(A) (1968) 1078.

[184] V.A. Verkhotin, V.V. Rode, S.P. Rafikov, Vysokomolek. Soed. IX (1967) 847.

[185] A. Ballistreri, S. Toti, P. Maravigna, G. Montaudo, E. Scamporrino, J. Polym. Chem. Ed. 18 (1980) 1923.

[186] A. Ballistreri, S. Toti, P. Maravigna, G. Montaudo, E. Scamporrino, J. Polym. Sci. Polym. Chem. Ed. 19 (1981) 1679.

[187] A. Ballistreri, S. Toti, P. Maravigna, G. Montaudo, E. Scamporrino, J. Polym. Sci. Polym. Chem. Ed. 20 (1982) 1685.

[188] A. Ballistreri, D. Garozzo, G. Montaudo, Macromolecules 17 (1984) 1312.

[189] A.A. Berlin, A.M. Dubinskaya, Vysokomolek. Soed. I (1959) 1678.

[190] A.N. Novikov, G.S. Gol'din, L.S. Baturina, Perkhlorsiloksany. Poluchenie i svoistva, Moskva, NIITEKhIM, 1985, S. 20.

[191] C. Somiesky, Chem. Ber. 56 (1923) 132.

[192] M.I. Rogovik, Z.L. Novitsky, P.D. Romanenko, Deposited manuscript No 2802/79, Chercassy, ONIITEKhIM, 1979.

[193] G.D. Cooper, A.R. Gilbert, J. Am. Chem. Soc. 82 (1960) 5042.

[194] G.S. Gol'din, L.S. Baturina, S.G. Fedorov, A.N. Novikova, T.N. Pushkova, Zh. Obshch. Khim. 50 (1980) 2627.

[195] H. Reiboldt, W. Wisfeld, J. Am. Chem. Soc. 57 (1935) 197.

[196] W.C. Schumb, C.H. Klein, J. Am. Chem. Soc. 59 (1937) 261.

[197] W.C. Schumb, C.M. Saffer, J. Am. Chem. Soc. 61 (1937) 363.

[198] W.C. Schumb, Chem. Rev. 31 (1942) 587.

[199] M.G. Voronkov, B.N. Dolgov, N.A. Dmitrieva, Dokl. Akad. Nauk SSSR, 84 (1952) 959; Inventor's Certificate 451172/344, Byull. Izobr. (1955) 13.

[200] M.G. Voronkov, Yu.I. Khudobin, Izv. Akad. Nauk SSSR Otd. Khim. Nauk (1956) 805.

[201] M.G. Voronkov, Yu.I. Khudobin, Izv. Akad. Nauk SSSR Otd. Khim. Nauk (1956) 713.

[202] B.N. Dolgov, S.N. Borisov, M.G. Voronkov, Zh. Obshch. Khim. 27 (1957) 716.

[203] B.N. Dolgov, S.N. Borisov, M.G. Voronkov, Zh. Obshch. Khim. 27 (1957) 2692.

[204] M.G. Voronkov, V.E. Puzanova, S.F. Pavlov, E.I. Dubinskaya, Izv. Akad. Nauk SSSR Ser. Khim. (1975) 448.

[205] M.G. Voronkov, E.I. Dubinskaya, S.F. Pavlov, Seventh Internat. Conference on Organometallic Chemistry, Abstracts, Venice, 1975, p. 155.

[206] M.G. Voronkov, E.I. Dubinskaya, S.F. Pavlov, V.G. Gorokhova, Izv. Akad. Nauk SSSR Ser. Khim. (1976) 2355.

[207] M.G. Voronkov, E.I. Dubinskaya, V.G. Komarov, S.F. Pavlov, Zh. Obshch. Khim. 46 (1976) 1908.

[208] M.G. Voronkov, V.G. Komarov, A.I. Albanov, I.M. Korotaeva, E.I. Dubinskaya, Izv. Akad. Nauk SSSR Ser. Khim. (1978) 1415.

[209] M.G. Voronkov, V.G. Komarov, A.I. Albanov, E.I. Kositsina E.I. Dubinskaya, Izv. Akad. Nauk SSSR Ser. Khim. (1978) 1692.

[210] V.A. Pestunovich, L.P. Petukhov, V.I. Rakhlin, B.Z. Shterenberg, R.G. Mirskov, M.G. Voronkov, Dokl. Akad. Nauk SSSR 263 (1987) 904.

[211] M.G. Voronkov, E.I. Dubinskaya, V.G. Komarov, Zh. Obshch. Khim. 60 (1990) 1355.

[212] G.M. Telysheva, R.E. Pankova, A.V. Novikov, E.I. Dubinskaya, M.G. Voronkov, YIII Internat. Symp. Fundamental Research of Wood Abstracts, Warsaw, 1990, p. 90.

[213] M.G. Voronkov, E.I. Dubinskaya, J. Organomet. Chem. 410 (1991) 13.

[214] R. Piekoš, A. Radecki, Roczn. Chem. 36 (1962) 1303.

[215] H.H. Anderson, D.L. Seaton, R.P.T. Radnicki, J. Am. Chem. Soc. 73 (1951) 2144.

[216] B. Sternbach, A.C. MacDiarmid, J. Am. Chem. Soc. 83 (1961) 3384.

[217] W. Ando, M. Ikeno, Chem. Lett. (1980) 1255.

[218] D. Grafslein, J. Am. Chem. Soc. 77 (1955) 6650.

[219] W. Ando, M. Ikeno, Tetrahedron Lett. 51 (1979) 4941.

[220] H.H. Anderson, J. Am. Chem. Soc. 81 (1959) 4786.

[221] H.J. Emeleus, A.G. MacDiarmid, A.G. Maddoc, J. Inorg. Nucl. Chem. 1 (1955) 194.

[222] H.J. Emeleus, M. Onyszchuk, W.Z. Kuchen, Z. Anorg. Chem. 283 (1956) 74.