Intermediates of chemical assembling of oligoorganosiloxanes in hydrolysis of organochlorosilanes

E. A. Chernyshev, P. V. Ivanov,★ and D. N. Golubykh

M. V. Lomonosov Moscow State Academy of Fine Chemical Technology,
86 prosp. Vernadskogo, 117571 Moscow, Russian Federation.
Fax: +7 (095) 246 4670. E-mail: ipvdim@unesco.mitht.rssi.ru

The mechanism of the formation of oligoorganosiloxanes during the hydrolysis of organochlorosilanes was considered. A comparative estimation of a relationship of the degree of conversion of the monomer *vs.* degree of conversion of functional groups in the homo- and heterofunctional condensation and partial hydrolysis of organochlorosilanes was performed for the first time. In the hydrolysis of diorganodichlorosilanes with either an excess or a deficiency of water, the homofunctional condensation of diorganosilanediols is not the main mode for the chemical assembling of oligoorganosiloxanes. The main intermediates in the route of oligoorganosiloxane formation during organochlorosilane hydrolysis are the incomplete hydrolysis products (organochlorohydroxysilanes). Experimental data suggest that the chemical assembling of oligoorganosiloxanes occurs *via* the mechanism of organochlorohydroxysilane heterocondensation under usually used conditions of organochlorosilane hydrolysis.

Key words: hydrolysis, organochlorosilanes, organosilanols, organochlorohydroxysilanes, homofunctional condensation, heterofunctional condensation, diorganosilanone.

The hydrolytic polycondensation (HPC) of organochlorosilanes is the main way for the preparation of polyorganosiloxanes with various compositions and structures. Many significant details of this very complicated process still remain unstudied. It is difficult to study HPC of organochlorosilanes, as well as majority of polycondensation processes, because of high rates of the initial stages of the synthesis and complicated analysis of the product composition. In addition, HPC of organochlorosilanes is characterized by several specific features. First, this is a limited mutual solubility of water and organochlorosilanes resulting in the heterophase character of the process. Second, the HPC of organochlorosilanes includes stages of the origination of reaction sites and intermediates of different types, which can determine the different characters of chemical assembling of oligomeric molecules of organosiloxanes.

The formation of the siloxane bond in HPC, for example, diorganodichlorosilanes, can be described by reactions (1)—(8) (Scheme 1).*

In addition, exchange reactions between chloro- and hydroxyl-containing compounds,[1,2] are also possible, *e.g.*, according to Eq. (9).

Reaction (9) can affect the microunit character of polyorganosiloxanes obtained by the cohydrolysis of organochlorosilanes.

It is seen from Scheme 1 that the reaction sites of three types can participate in oligoorganosiloxane formation: $\equiv$Si—Cl, $\equiv$Si—OH, and =Si=O, and the first two are involved in homofunctional condensation (HMFC) (Eqs. (3), (5), and (7)) and heterofunctional condensation (HTFC) (Eqs. (4) and (6)), which occur *via* the mechanism of nucleophilic substitution S_N2-Si and are reversible, irreversible, or autocatalytic,[3] depending on the conditions. The reaction site of the third type is involved in polymerization (reaction (8)). Based on the general regularities of S_N2 substitution at the silicon atom, we can arrange the presented reaction in an order of decreasing their rate constants: hydrolysis $\gg$ HTFC > HMFC.[3]

If the hydrolysis of R_nSiCl_{4-n} is performed with a water excess, it is evident that at the indicated ratio of hydrolysis to HTFC rate constants during the time of $R_nSi(OH)_{4-n}$ formation the fraction of HTFC reactions (see Scheme 1, Eqs. (4) and (6)) is insignificant. Based on this, we believe that the commonly accepted concept is valid: under the conditions of a water excess, organosiloxanes are synthesized *via* the route of the HMFC of silanols (Eqs. (3), (5), and (7)). It is likely that this is why the HTFC reactions in the HPC of organochlorosilanes are ignored in most cases.

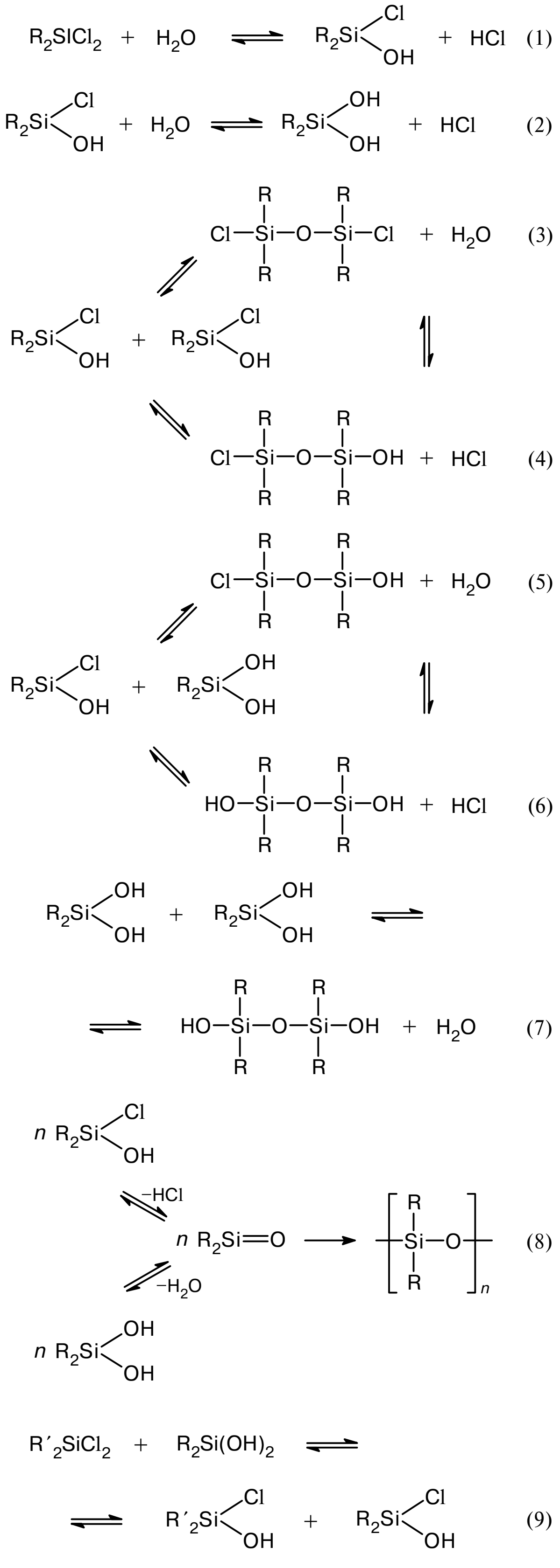
The studies of the macrokinetics of the HPC of organochlorosilanes showed that this process is heterophase due to the limited mutual solubility of the reactants, water and organochlorosilane.[4] The condition of a water excess over organochlorosilane is accomplished in the aqueous phase of the reaction system in which the amount of organochlorosilane is negligible and does not substantially contribute to the formation of oligo-

---

* For simplification, we did not present all possible variants for dimer formation in the scheme.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 1909—1919, November, 2001.

Scheme 1



organosiloxanes. The main amount of organochlorosilane is distributed into the organic phase of the system. At the really used ratios of water, organochlorosilanes, and the solvent, organic phases of the reaction system are characterized by a water deficiency with respect to organochlorosilane. In this case, some unreacted organochlorosilane can react (HTFC) with the $R_nSiCl_mOH_{4-n-m}$ compounds that formed in the organic phase.* It is very difficult, in this case, to estimate the relative contribution of the HMFC and HTFC reactions to the process of oligoorganosiloxane preparation.

As for the third way for oligoorganosiloxane synthesis by the polymerization of $R_2Si{=}O$, note that, unlike combinations of various reaction fragments in the formation of oligomeric molecules during HMFC and HTFC, unit-to-unit assembling of macromolecules can occur in this ultimate case. A possibility of the unit-to-unit assembling of polyorganosiloxanes during $R_2Si{=}O$ polymerization has been discussed previously,[5] and presently this problem has become urgent again.[6—8] In connection with the aforesaid, it seemed reasonable to analyze available published data with the purpose for revealing distinctions in the regularities of chemical assembling of oligomeric organosiloxane molecules *via* the mechanisms of HMFC, HTFC, and $R_2Si{=}O$ polymerization.

Stage of the formation of reaction sites

The first stage of hydrolytic condensation is hydrolysis resulting in the appearance of the reaction sites >SiCl(OH) and $>Si(OH)_2$ (see Scheme 1, Eqs. (1) and (2)). These compounds are highly reactive to impede their synthesis and isolation in the pure state.

Organochlorohydroxysilanes $Me_2Si^{35}ClOH^+$ and $Me_2Si^{37}ClOH^+$ were first observed by mass spectrometry.[5] It has been established[5] that these compounds are present in a high concentration (35%) in the products of incomplete hydrolysis. Much later high concentrations (75% of the initial concentration of $PhSiCl_3$) of the $PhSiCl_2(OH)$, $PhSiCl(OH)_2$, and $PhSi(OH)_3$ compounds have been detected[9] in the hydrolysis products of phenyltrichlorosilane by IR spectroscopy. It has been shown[9] that, as well as in earlier studies,[10—12] the first Cl atom is hydrolyzed most rapidly. Therefore, intermediates of the $R_nSiCl_m(OH)_{4-n-m}$ type are accumulated during some time interval.

Taking into account evident difficulties of the isolation of the intermediate compounds and study of their successive transformations (see Scheme 1), we may conclude that a comparison of the plots of the monomer conversion *vs.* degree of conversion of functional groups is one of few possible methods for the detection of distinctions in the regularities of the formation of oligomeric molecules *via* the above indicated mechanisms

---

* Hydrolysis due to coming in of water from the aqueous phase is limited by diffusion.

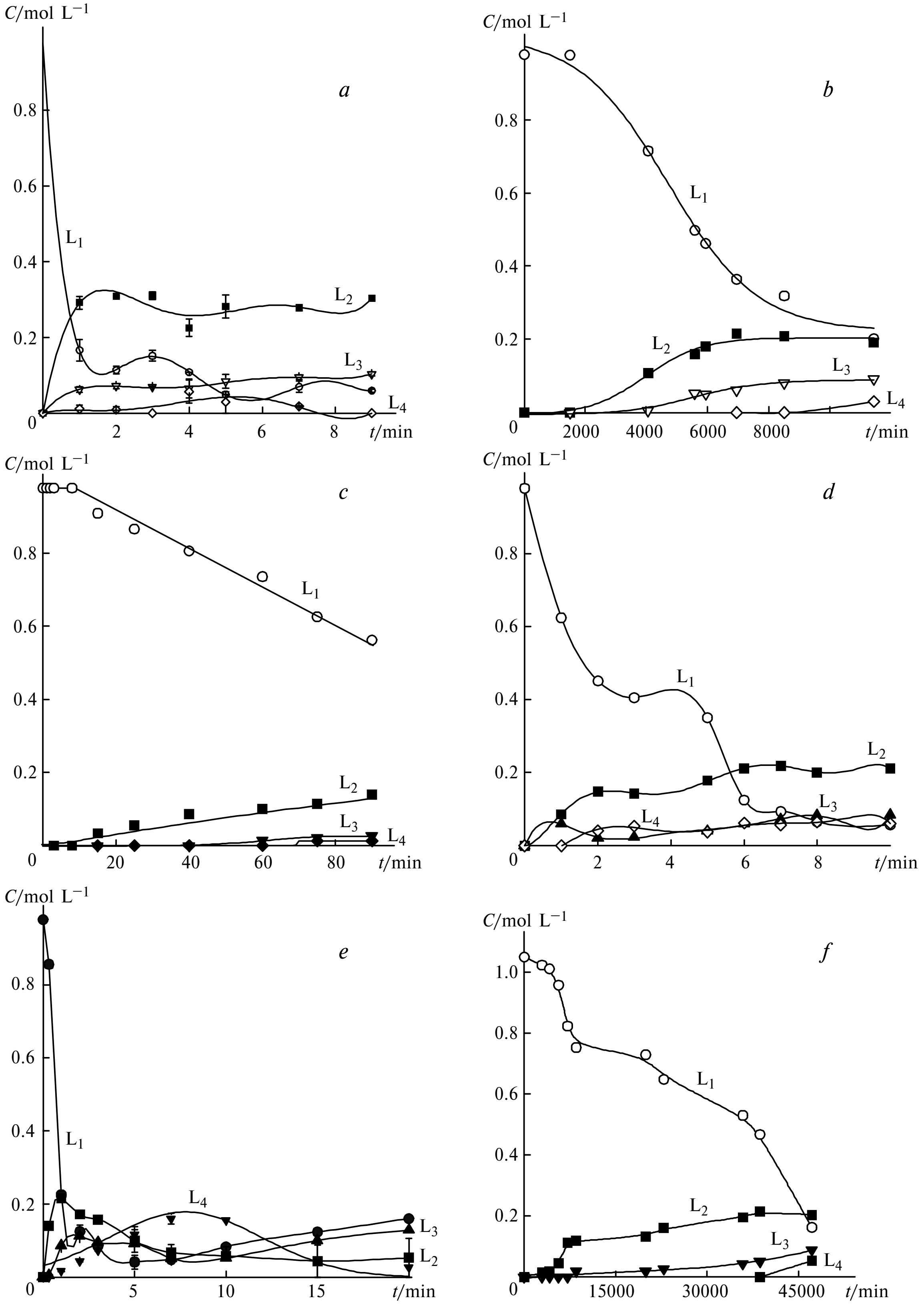


Fig. 1. Types of kinetic curves of the consumption of $MePhSi(OH)_2$ and the formation of the condensation products L_n = HO—$[SiMePhO]_n$—H in aqueous-acetone (*a*—*e*) or aqueous-dioxane (*f*) solutions at pH = 0.0 (*a*), 5.9 (*b*), 10 (*c*), 12 (*d*), 13 (*e*), and 4.5 (*f*); horizontal strokes in curves (*a*) indicate the confidence interval of concentration values.

(HMFC, HTFC, and $R_2Si=O$ polymerization). This is precisely the aspect in which we consider these processes.

Homofunctional condensation of organosilanols

The homofunctional condensation of organosilanols was of great interest as the main reaction of polyorganosiloxane formation.[13—17] The kinetics of the HMFC of silanols has previously being studied[17,18] and is under study presently. Studies in this area have been analyzed in detail.[4]

The procedures of studying the kinetics of HMFC of silanols based on the measurement of the amount of water evolved upon polycondensation[13,19—21] or on the detection of absorption bands of the ≡SiOSi≡ or ≡SiOH groups in the IR spectra have the whole series of restrictions: they do not allow one to study the condensation of $R_2Si(OH)_2$ at high water concentrations and, chiefly, do not allow monitoring of the composition of the condensation products of $HO(SiR_2O)_nH$ because these methods determine the total number of the ≡SiOH and ≡SiOSi≡ groups or the total amount of the evolved water. Therefore, the application of methods of this type is restricted only by a low conversion of the monomer (15—25%). Nevertheless, these works[19—21] considerably contributed to the study of the mechanism of organosilanol polycondensation: the orders with respect to monomer, acidic and basic catalysts were determined, and the plots of the condensation rate *vs.* water concentration, temperature, and nature of the solvent and substituent at the silicon atom were obtained. Many features in the process of organosilanol condensation remain unclear and, above all, the principle of the formation of the polymeric chain remains nonrevealed because the composition of the condensation products is poorly studied.

Liquid chromatography (TLC and HPLC) allows monitoring concentrations of all products of the HMFC of silanols up to the achievement of deep degrees of conversion of the monomer.[4,22,23] The application of quantitative methods of TLC and HPLC for monitoring the product composition of $R_2Si(OH)_2$ HMFC made it possible to reveal the complicated character and variety of types of kinetic curves of $R_2Si(OH)_2$ consumption and $HO(SiR_2O)_nH$ formation[4,22,24] (Fig. 1).

The general peculiarity of the kinetic curves of monomer consumption during both the acid- and base-catalyzed HMFC is their complicated, "stepped" profile characterized by segments of reaction retardation and acceleration, induction period, and segments corresponding to the autocatalysis phenomenon (Fig. 2). We detected the induction period for the HMFC of $RR'Si(OH)_2$ in a wide interval of water concentrations (0—16 mol L^{-1}) under the conditions of both acidic and alkaline catalysis. The HMFC of $PhSi(OH)_3$ in various solvents is characterized by the most pronounced induction period (see Fig. 2).

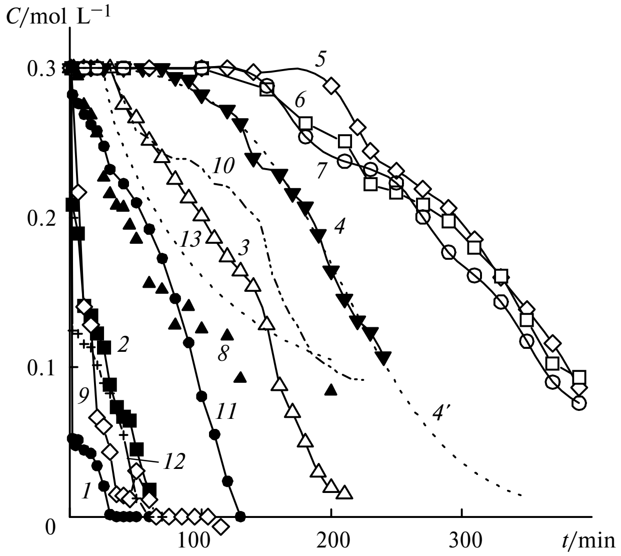


Fig. 2. Kinetic curves of $PhSi(OH)_3$ condensation, C_0 = 0.3 mol L^{-1}, dioxane—water, $[H_2O]_0$ = 16 (*1—9*) or 8.75 mol L^{-1} (*10*), pH = 1.1 (*1*), 1.4 (*2*), 2.0 (*3*), 2.5 (*4*), 4.0 (*5*), 5.0 (*6*), 6.0 (*7*), 7.0 (*8*), 9.0 (*9*), 7.0 (*10*); acetone—water, pH = 2.0 (*11*); DMF—water, pH = 2.0 (*12*); in the absence of the catalyst in anhydrous acetone (*13*); *4′*, data approximation by the integral equation of the autocatalytic reaction rate of a first order.

The oscillatory kinetic curves were also observed in the study of $R_2Si(OH)_2$ HMFC.[24] We detected the high-amplitude concentration oscillations of $PhSi(OH)_3$ (Fig. 3, *a*) and tetrahydroxytetraphenylcyclotetrasiloxane at low concentrations of water and the acidic catalyst. The experimentally observed fast mutual transformation in the absence of the catalyst

$$n\ \mathrm{PhSi(OH)_3} \rightleftharpoons \mathrm{HO[PhSi(OH)O]}_n\mathrm{H}$$

indicates the unusually high lability of the siloxane bond and its ability to the fast rearrangement.

We also detected[24] the oscillation character of the HMFC of $Et_2Si(OH)_2$ at high concentrations of water and the catalyst. The concentration oscillations were also observed for the acid- and base-catalyzed HMFC of 1,3-tetramethyldisiloxanediol (Fig. 3, *b*). The results of studying the HMFC of $R_2Si(OH)_2$ were analyzed in detail.[4]

The dependence of the degree of conversion of the monomer (X_M) on the degree of conversion of functional groups (X_f) was used as a quantitative criterion of the chemical assembling of oligoorganosiloxanes.[25] The dependence $X_M = 2X_f$ (Fig. 4, curve *1*) corresponds to the ultimate case of the blocking (polycondensation) assembling of oligomeric molecules by duplication, and equality of the degree of conversion $X_M = X_f$ corresponds to unit-to-unit (polymerization) assembling or cyclization (see Fig. *4*, line *2*). Figure 4 presents the plots $X_M = f(X_f)$, which include data of many series of experiments (as a whole, 500 experimental points) on the

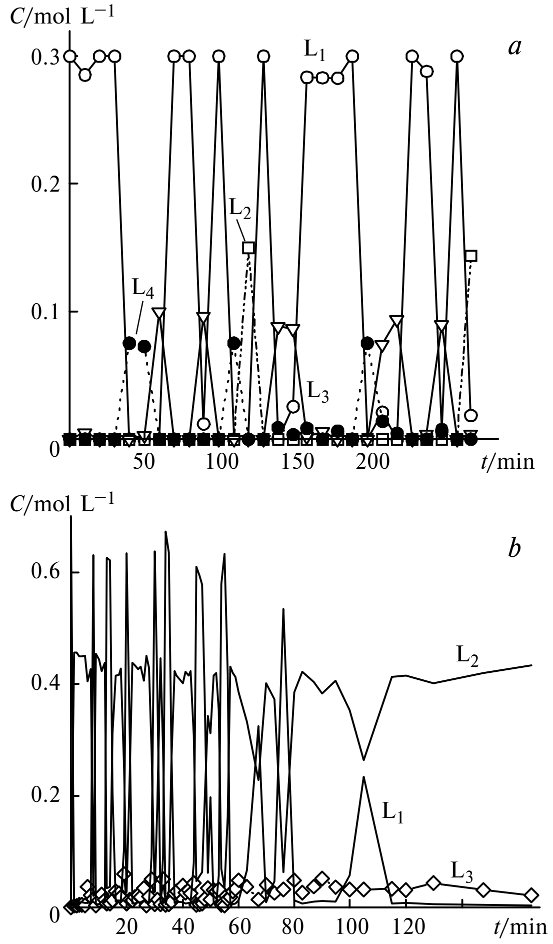


Fig. 3. Oscillatory kinetic curves of condensation of $PhSi(OH)_3$ without the catalyst in dioxane (*a*) and tetramethyldisiloxane-1,3-diol in an acetone—water medium at pH = 14 (*b*).

HMFC of $Me_2Si(OH)_2$, $Et_2Si(OH)_2$, and $MePhSi(OH)_2$ performed at different initial concentrations of $R_2Si(OH)_2$ in the pH 1—14 interval in both water-organic (in mixtures of water with acetone, dioxane, and DMF, H_2O content 0.01—16 mol L^{-1}) and anhydrous media. When these factors are varied, the rate of $R_2Si(OH)_2$ HMFC changes by four to six orders of magnitude,[4] whereas the type of assembling of oligomeric molecules remains unchanged. Thus, the character of the $X_M = f(X_f)$ dependence (and, hence, the type of chemical assembling of molecules) is common for all considered variants of HMFC and slightly depends on the nature of substituents at the silicon atom, initial concentrations of the monomer, catalyst, and water, and the solvent nature.

Heterofunctional condensation of organosilanols with organochlorosilanes

The HTFC reaction of organosilanols with organochlorosilanes has been known long ago (1885) and is widely used in the synthesis of organosilicon oligomers and polymers with different compositions and structures.[26] Unlike the hydrolysis and HMFC of silanols, the HTFC of organochlorosilanes with silanols is virtually unstudied. The results of studying the kinetics and mechanism of the HTFC of only monofunctional organochlorosilanes with organosilanols are presently published.[27] Therefore, we will not consider them. Below we analyze the probability of HTFC under the conditions of organochlorosilane HPC.

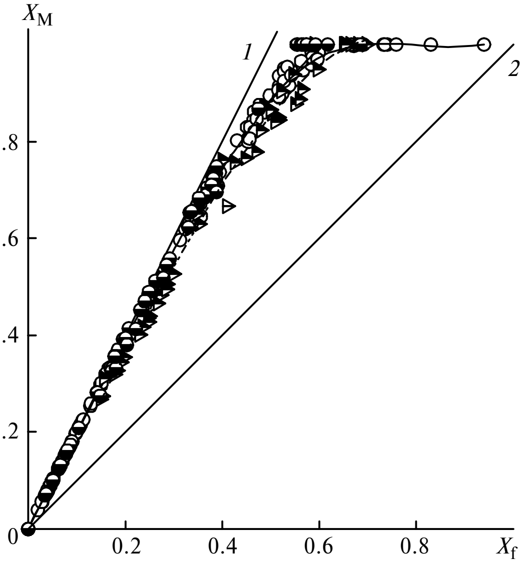


Fig. 4. Data array on the relationship of the degree of conversion (X_M) of $R_2Si(OH)_2$ *vs.* degree of conversion of functional groups (X_f) in aqueous-organic and anhydrous organic media for HMFC; curve *1* corresponds to doubling condensation, and *2* corresponds to the unit-to-unit assembling of molecules (polymerization).

In studying[10] the hydrolysis mechanism and the probability of the formation of the siloxane bond during the HTFC of the hydrolysis products with the initial chlorosilane, it is assumed that the HTFC reaction is the limiting stage

$$RSiCl_2OH + RSiCl_3 \rightarrow Cl_2Si(R)O(R)Cl_2 + HCl.$$

However, the authors[10] indicate that available experimental data are insufficient to conclude a substantial contribution of this reaction to the formation of oligoorganosiloxanes.

The kinetic measurements of the reaction of $PhSiCl_3$ and $PhSi(OH)_3$ were carried out[9] by the continuous flow method with the detection of the reaction products by IR spectroscopy. In the absence of HCl, $PhSiCl_3$ and $PhSi(OH)_3$ did not react for the time characteristic of the hydrolysis of $PhSiCl_3$ (~1 s). Since the main product at the end of $PhSiCl_3$ hydrolysis is $PhSi(OH)_3$, we concluded that the HTFC of $PhSiCl_3$ and $PhSi(OH)_3$ did not substantially contribute to the formation of organosiloxanes. However, at an initial concentration of HCl of 0.39 mol L^{-1} we detected a considerable decrease in the intensities of the signals from $PhSiCl_3$ and $PhSi(OH)_3$ in the IR spectrum. The half-reaction time of $PhSi(OH)_3$ in the reaction with $PhSiCl_3$ in the presence of HCl is 0.5 s in this case as well, whereas the half-reaction times of $PhSiCl_3$ and $PhSiCl_2(OH)$ in hydrolysis are equal to 0.0015 and 0.1 s, respectively. Therefore, the contribution of the HTFC of $PhSi(OH)_3$ with $PhSiCl_3$ to the consumption of the latter could barely be of a great significance. The absence of the HTFC of organochlorohydroxysilane and alcohol (without additives of hydrogen chloride) was also established for the alcoholysis of Ph_3SiCl.[28]

The contribution of HTFC for the hydrolysis of organochlorosilane in the gas phase is evaluated differently.[29] The authors[29] believe that the gas-phase HTFC of the initial organochlorosilane and organosilanol that formed is rapid. Unfortunately, they do not present arguments in favor of this conclusion. In several works, the conclusion about a considerable contribution of the HTFC of organochlorosilanols with organochlorosilane is based on the study of the composition of their hydrolysis products. So, qualitative analysis of the reactivity of the intermediate products of the cohydrolysis of phenyltrichlorosilane and diethyldichlorosilane with an insufficient amount of water suggested[30] that heterounit oligoorganosiloxanes are preferentially formed in the HTFC reaction of the reactive phenyldichlorosilanol with a less reactive and almost unreacted (in hydrolysis) diethyldichlorosilane.

The study of the cohydrolysis of trimethyl- and triethylchlorosilanes with a water excess in benzene showed[31] that the yield of the cocondensation product of $Me_3SiOSiEt_3$ was overestimated compared to that calculated taking into account a great difference between the HMFC constants of Me_3SiOH and Et_3SiOH (~600 : 1). It was assumed[31] that $Me_3SiOSiEt_3$ was formed at the interface in the HTFC reaction of trimethylsilanol with triethylchlorosilane, and $Me_3SiOSiMe_3$ and $Et_3SiOSiEt_3$ were formed according to HMFC in the aqueous and organic phases, respectively.

In studying[32] the cohydrolysis of methyldichlorosilane, dimethyldichlorosilane, and diphenyldichlorosilane with an equimolar amount of water, the authors replaced diphenyldichlorosilane by the product of its hydrolysis, diphenylsilanediol. This decreased the content of the phenylsiloxane units in the heterounit cyclosiloxanes. It can be assumed that the heterounit cyclosiloxanes are formed in the HTFC reaction of $MeHSi(OH)_2$ and $Me_2Si(OH)_2$ with Ph_2SiCl_2 rather than in the HMFC of $Ph_2Si(OH)_2$ with the silanols indicated.

The data presented indicate a noticeable contribution of HTFC to the preparation of the HPC products of organochlorosilanes, including organocyclosiloxanes, under the conditions of hydrolysis of organochlorosilanes with an insufficient amount of water or an excess of water when the solvent that is not mixed with water is used.

The problem on the role of HTFC in the formation of oligoorganosiloxanes during organochlorosilane HPC has been studied[3,4] in detail and systematically. It has been shown that during organochlorosilane HPC oligoorganosiloxanes are predominantly synthesized by the HTFC of the initial organochlorosilane with the products of its hydrolysis, organosilanols. This is reasoned by both kinetic and macrokinetic factors.[4] Let us consider the main experimental facts that prove the prior role of HTFC in the formation of oligoorganosiloxanes.

It has been established[22] that α,ω-dihydroxysiloxanes (for example, tetramethyltetraphenyltetrasiloxane-1,7-diol) are formed in the HPC of $MePhSiCl_2$ (pH = 7—8) in 70—90% yield for 10—15 s, whereas at the HMFC of $MePhSi(OH)_2$ under similar conditions, tetramethyltetraphenyltetrasiloxane-1,7-diol is obtained in 40% yield only after 190 h! It is also found that the composition of the HPC products of $MePhSiCl_2$ depends on several factors that have no effect on the HMFC of organosilanols: the intensity and order of mixing of reactants,[33] the ratios of volumes and compositions of the coexisting phases.[34] The characteristic regularity of heterocondensation is manifested in the variation of these factors: the degree of polymerization of macromolecules depends on the ratio of functional groups.

In the case of the HPC of organochlorosilanes, the reactants are the initial organochlorosilane R_nSiCl_{4-n} and the products of its hydrolysis $R_nSiCl_m(OH)_{4-n-m}$. Due to a deficiency of water in the organic phase, the fraction of compounds with completely substituted chlorine atoms, $R_nSi(OH)_{4-n}$, is very low. Since the main amount of organochlorosilane is distributed into the organic phase, the main amount of the target product is also formed in this phase. Therefore, controling the composition of the products of the initial stages of organochlorosilane HPC is reduced, in essence, to controlling the composition of products of the partial hydrolysis of R_nSiCl_{4-n}.

Regularities of chemical assembling of oligoorganosiloxanes in the partial hydrolysis of organochlorosilanes

The most studies of the partial hydrolytic condensation (PHC) of organochlorosilanes is related to the early period of development of chemistry of organosilicon compounds. It is convenient to consider specific features of the hydrolysis of organochlorosilanes, under the conditions of water amount insufficient for the complete substitution of functional groups, using α,ω-dichlorodiorganosiloxanes $Cl(SiRR'O)_{n-1}SiRR'Cl$ as an example. This is due to the fact that these oligomers (unlike most their hydroxyl-containing analogs $HO(SiRR'O)_nH$) can be isolated by rectification or detected by GLC[35] and NMR.[36] The methodical aspects of the PHC of organochlorosilanes have been published previously.[4]

The main products of the partial hydrolysis of diorganodichlorosilanes (at the ratio H_2O : $RR'SiCl_2$ = 1 : 2 and the concentration of the organic solvent 5—52 wt.%) are the unreacted $RR'SiCl_2$ (22—48 wt.%), low-molecular α,ω-dichlorodiorganosiloxanes $L_n \equiv Cl(SiRR'O)_{n-1}SiRR'Cl$ at n = 2, 3 (47—76 wt.%), and organocyclosiloxanes $D_n \equiv (RR'SiO)_n$ at n = 3, 4 (to 2 wt.%).

Analysis of published data shows that the composition of the PHC products differs from the statistical Flory distribution, and this difference increases with a decrease in the solvent concentration in the system. The composition of the PHC products of the $RR'SiCl_2$ compound can deviate from the statistical value due to a gradual decrease in the reactivity of the oligomers that formed.[35] We have found that another and, perhaps, more important reason is the influence of the macroscopic factors: the heterophase character of the PHC process, the order and intensity of mixing reactants.[4,37]

The formation of oligosiloxanes during the partial hydrolysis of $RR'SiCl_2$ is usually described by the scheme corresponding to the HMFC mechanisms of hydroxyl-containing derivatives, although it sometimes indicates a possibility of HTFC.[38—40] For example it is assumed that, in the presence of metal oxides, hydrolysis occurs due to water evolved, *e.g.*, in the reaction[39]

$$Fe_2O_3 + 6\ HCl \rightarrow 2\ FeCl_3 + 3\ H_2O.$$

In this case, the scheme of the formation of dichlorodiorganosiloxanes corresponds to the HTFC mechanism[39]

$$Me_2SiCl_2 + H_2O \rightarrow Me_2Si(OH)Cl + HCl,$$
$$ClMe_2SiOH + Me_2SiCl_2 \rightarrow$$
$$\rightarrow ClMe_2SiOSiMe_2Cl + HCl,$$
$$ClMe_2SiOH + ClMe_2SiOSiMe_2Cl \rightarrow$$
$$\rightarrow Cl(Me_2SiO)_2SiMe_2Cl + HCl.$$

The same mechanism (*i.e.*, HTFC) is assumed for partial hydrolysis in the liquid phase,[30] vapor phase,[29] and at −70 °C.[12] The general feature of a few studies of the partial hydrolysis of organochlorosilanes is that the proposed mechanism of dichlorodiorganosiloxane formation is presented without proofs, and the choice between HMFC and HTFC is based on the intuitive preference of authors. The plots of the degree of conversion of the monomer (X_M) *vs.* degree of conversion of functional groups (X_f) were not analyzed.

Using published data by independent authors,[35,41—46] we obtained the plots $X_M = f(X_f)$ (Fig. 5). The compositions of the PHC products are described by the same dependence $X_M = f(X_f)$ (see Fig. 5, curve *1*). As in the case of the HMFC of organosilanols, the $X_M = f(X_f)$ dependence (see Fig. 5, curve *1*) is general for organochlorosilanes with different substituents at the silicon atom. Note a coincidence of the independent results obtained in different times, at different concentrations, in the liquid and gas phases. For comparison, Fig. 5 contains the plots $X_M = f(X_f)$ for the HMFC of $Me_2Si(OH)_2$ (curve *2*) and $MePhSi(OH)_2$ (curve *3*). Taking into account that the $X_M = f(X_f)$ plots for the HMFC of two silanols also unify the data obtained in different solvents in a wide interval of catalyst concentrations, we can assume that the distinction in the $X_M = f(X_f)$ plots for HMFC and PHC indicates the different characters and mechanisms of chemical assembling of oligomeric molecules.

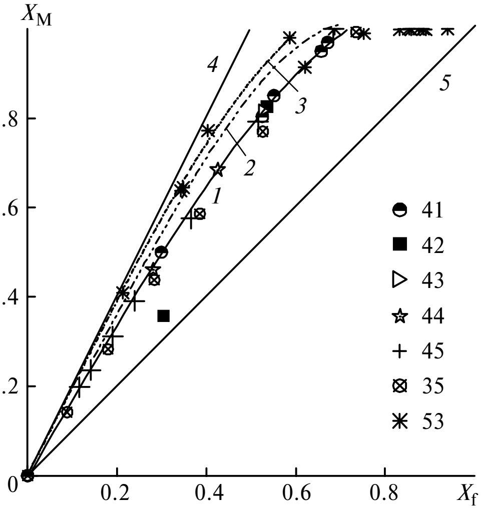


Fig. 5. Plots of the degree of conversion of the monomer (X_M) *vs.* degree of conversion of functional groups (X_f) for the partial hydrolysis of R_2SiCl_2 (calculated from experimental data of references indicated in figure) (*1*), for HMFC of $Me_2Si(OH)_2$ (*2*) and for HMFC of $MePhSi(OH)_2$ (*3*); line *4* corresponds to doubling condensation, and *5* is unit-to-unit assembling.

In order to confirm this assumption, the partial hydrolysis of $MePhSiCl_2$, its HTFC with $MePhSi(OH)_2$, and HMFC of the latter were studied in combination.[7,8,47] The studies were carried out under similar conditions: in dioxane at the same concentrations of monomers and water; the HMFC of $MePhSi(OH)_2$ was studied in dioxane at the HCl concentration (≥2 mol L^{-1}) corresponding to the amount of hydrogen chloride evolved in HTFC and PHC. The molar ratio of water (or $MePhSi(OH)_2$) to $MePhSiCl_2$ was varied from 0.1 to 1.0. The composition of the HTFC and PHC products was analyzed after 60 s after the reactants were mixed. Figure 6 presents the plots of the product compositions (*S*) and degree of conversion of monomers (X_M) *vs.* degree of conversion of functional groups (X_f) in the HMFC of $MePhSi(OH)_2$, PHC of $MePhSiCl_2$, and HTFC of $MePhSi(OH)_2$ with $MePhSiCl_2$. It is seen that the compositions of the PHC and HTFC products are close to each other and sharply differ from the composition of the HMFC products of $MePhSi(OH)_2$. The distinction of the HMFC of $MePhSi(OH)_2$ is the fast disappearance of the $MePhSi(OH)_2$ monomer and the formation of a great amount of dimethyldiphenyldisiloxane-1,3-diol (see Fig. 6, *a*—*c*). In HTFC the monomer is completely consumed at X_f = 0.7, and in HTFC and PH, at X_f = 1.

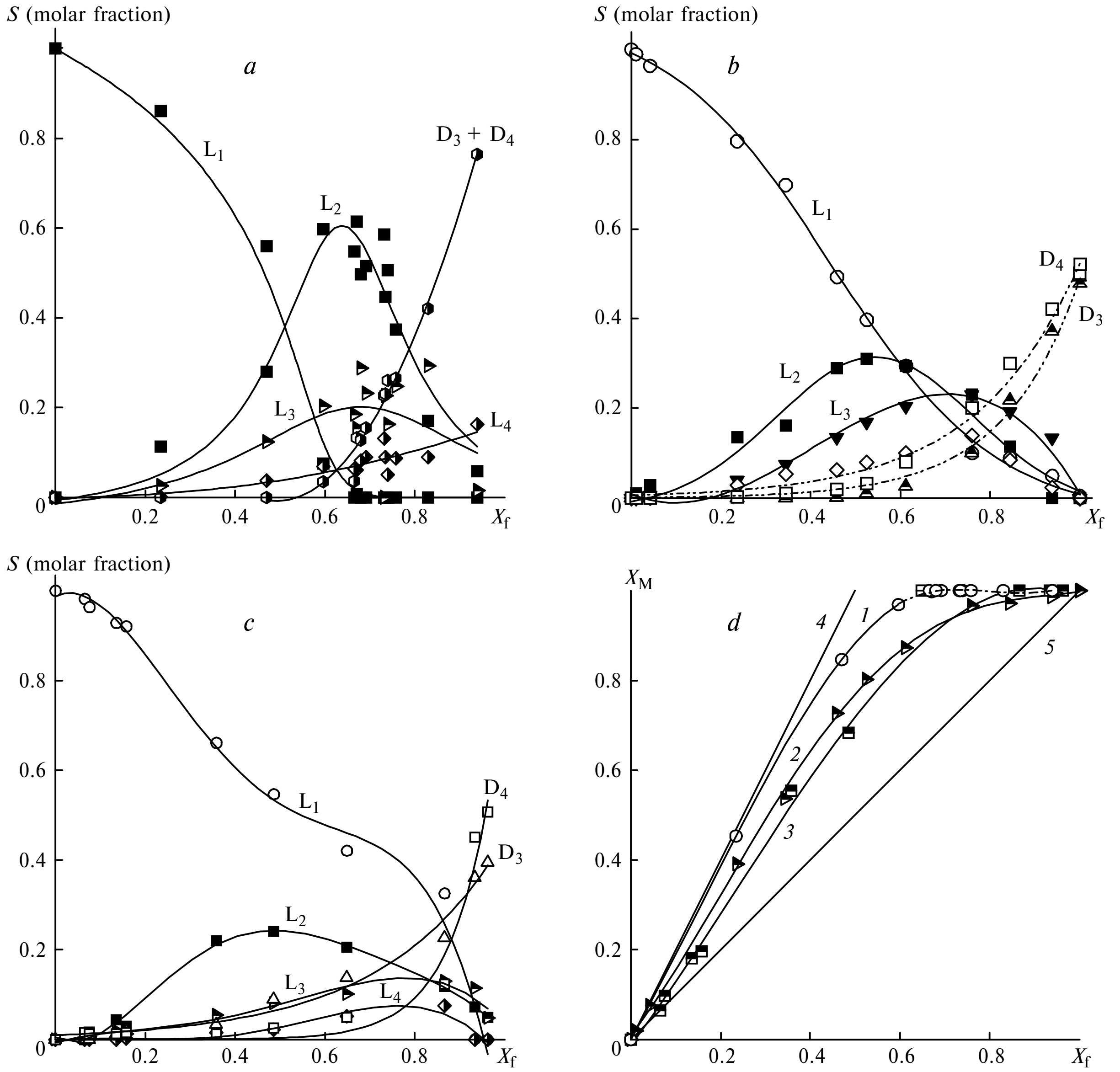


Fig. 6. Plots of the composition of the products (S) (*a—c*) and degree of conversion of the monomer (X_M) (*d*) *vs.* degree of conversion of functional groups (X_f) in HMFC processes (*a*; *d*, curve *1*), PH (*b*; *d*, curve *2*), and HTFC (*c*; *d*, curve *3*); line *4* (*d*) corresponds to doubling condensation and *5* (*d*) corresponds to unit-to-unit assembling.

This is reflected in the distinction of the $X_M = f(X_f)$ plots (see Fig. 6, *d*).

The fact of the accumulation of dimethyldiphenyldisiloxane-1,3-diol in the reaction system of HMFC agrees with data of the kinetic studies of HMFC. It is established that, depending on the conditions, the rate constant for tetramethyldisiloxane-1,3-diol is 3—35-fold lower than that for dimethylsilanediol[16,21]; the rate constant of dimethyldiphenyldisiloxane-1,3-diol condensation is tenfold lower than that for methylphenylsilanediol.[4] After the "fast" disappearance of the $MePhSi(OH)_2$ molecules, oligomeric molecules are formed by blocking assembling (of the "*n*-mer + *m*-mer" type) close to the ultimate case, duplication of molecules. In the case of PHC and HTFC, the $X_M = f(X_f)$ plots are close to that for unit-to-unit assembling of molecules.

The distinction in the HMFC processes, on the one hand, and the PHC and HTFC processes, on the other hand, is also manifested in the time factor. For example, for PHC and HTFC the high yield of organocyclosiloxanes at $X_f = 1$ is achieved for 60 s, whereas for HMFC the 80% conversion of the monomer to cyclosiloxane requires more than 2.5 h. In addition, the quantitative (100%) formation of organocyclosiloxanes by the condensation of α,ω-dihydroxydiorganosiloxanes during PHC and HTFC is impossible because a deficiency of water in the system (see above). Thus, the formation of oligomers during the PHC of $MePhSiCl_2$

occurs differently than during HMFC and almost similarly with the HTFC of $MePhSiCl_2$ with $MePhSi(OH)_2$. At the same time, the coincidence of the plots of the compositions of the PHC and HTC products is rather unexpected because dichlorotrisiloxane rather than dichlorodisiloxane must be the main products in the reaction of $MePhSiCl_2$ with $MePhSi(OH)_2$ (see Fig. 6, *c*).

$$MePhSiCl_2 + MePhSi(OH)_2 \rightarrow$$
$$\rightarrow ClSiMePhOSiMePhOH + HCl$$
$$ClSiMePhOSiMePhOH + MePhSiCl_2 \rightarrow$$
$$\rightarrow Cl(SiMePhO)_2SiMePhCl + HCl$$

The formation of dichlorodisiloxane can be explained by the formation of MePhSi(OH)Cl *via* reversible reactions (see Scheme 1, Eqs. (2) and (9)) followed by HTFC with $MePhSiCl_2$. In this case, similarity of the PHC and HTFC processes is due to the common intermediate MePhSi(OH)Cl in the route of oligoorganosiloxane synthesis.

Third way of the formation of polyorganosiloxanes

A possibility of the preparation of polyorganosiloxanes through the stage of the appearance of organosilanones has been considered previously.[5] In the case of the hydrolysis of organochlorosilanes with a water excess, the synthesis of polyorganosiloxanes was assumed to occur through the intramolecular dehydration of $R_2Si(OH)_2$ to form $R_2Si=O$ followed by its polymerization (see Scheme 1, Eq. (8)). However, the study of the hydrolysis products of Me_2SiCl_2 with water in the chamber of a mass spectrometer showed that the content of $Me_2Si=O$ in them was only 1.3%, whereas the content of $Me_2Si(OH)Cl$ was 35%. It follows from published data[5] that the authors ignored the probability of intramolecular dehydrochlorination in the $R_2Si(OH)Cl$ molecule.

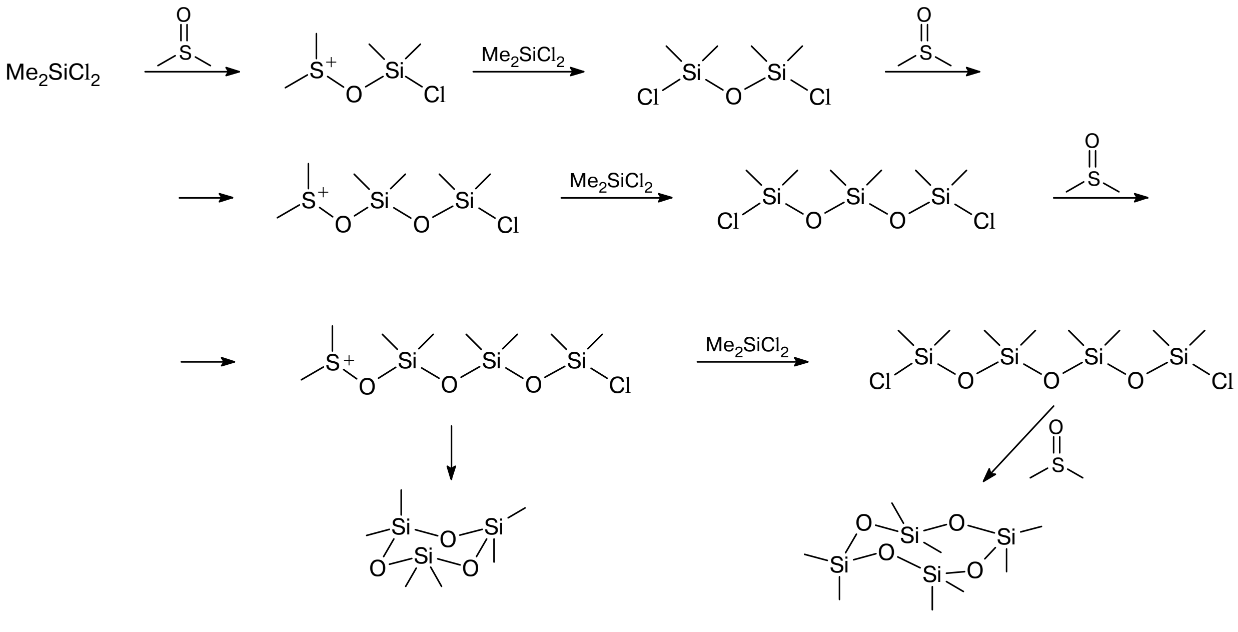
In the recent time, a possibility of the formation of polyorganosiloxanes through organosilanones $R_2Si=O$ by their polymerization or insertion into the available —Si—O—Si— units is being studied by several researchers.[46,48–51] Materials about the key role of $R_2Si=O$ in the HPC of organochlorosilanes have recently been presented.[6]

One of the methods for diorganosilanone generation is the reaction of R_2SiCl_2 with DMSO.[46] Reagent-traps are usually used to prove the formation of $R_2Si=O$ and its participation in the formation of the siloxane bond.[52] For example, based on the preparation of α,ω-hexamethyloligodimethylsiloxanes $Me_3SiO(SiMe_2O)_nSiMe_3$ (n = 3—10) by the reaction of diorganodichlorosilanes with DMSO, the authors[48] concluded that dialkylsilanone appeared in this reaction gives organocyclosiloxanes or is inserted into cyclic and linear organosiloxanes.

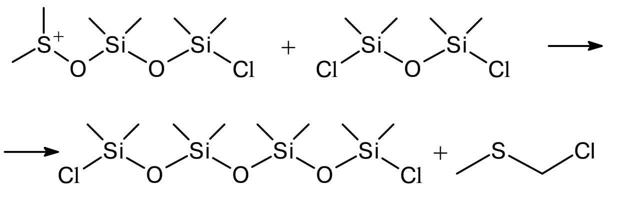
The role of $R_2Si=O$ as an intermediate in the synthesis of oligoorganosiloxanes was not confirmed by the study[53] of the reaction of Me_2SiCl_2 with DMSO, and the scheme of the unit-to-unit assembling of oligoorganosiloxanes involving no dimethylsilanone was proposed[53] (Scheme 2).

The reaction of DMSO with mixtures of Me_2SiCl_2 and 1,5-dichlorohexamethyltrisiloxane (L_3) with different compositions did not increase the yield of 1,7-dichlorooctamethyltetrasiloxane and octamethylcyclotetrasiloxane, as it was expected for the insertion of dimethylsilanone into L_3 and into D_3. This was an argument from the authors[53] against the participation of silanone in the formation of oligoorganosiloxanes in this process. The results of our processing of the experimental data of this study[53] are another argument against the

Scheme 2



scheme that implies the participation of $R_2Si=O$ in oligosiloxane assembling. Analysis of the obtained $X_M = f(X_f)$ dependence shows that in this process assembling of oligomeric molecules occurs block-to-block rather than unit-to-unit (see Fig. 5), as it should take place during $R_2Si=O$ polymerization but not in the way presented by the authors[53] (see Scheme 2). Taking into account this dependence, Scheme 2 should be supplemented by equations of the *n*-mer + *m*-mer type.



Contradictory data on the role of silanone in the formation of oligoorganosiloxanes were obtained by the study of the partial hydrolysis of Me_2SiCl_2 and $MePhSiCl_2$ and the condensation of the latter with $MePhSi(OH)_2$ in dioxane in the presence of an HCl acceptor.[7,8] It was found that oligomers $L_n \equiv Cl[SiMePhO]_{n-1}SiMePhCl$ are almost absent from the composition of the products of these reactions (Fig. 7), and only organocyclosiloxanes are present. The type of assembling is characterized by the $X_M = X_f$ dependence (correlation coefficient $r = 1$), indicating the polymerization character of the process. The same dependence is observed for low concentrations of HCl due to the use of a great amount of the solvent (≥80%)[8]. With an increase in the concentrations of HCl and reactants in the reaction mixture, the $X_M = f(X_f)$ dependence is gradually transformed from polymerization into polycondensation. These data suggest that, under different condition, either $R_2Si=O$ or $R_2Si(OH)Cl$, which are related by the equilibrium

$$R_2Si{=}O + HCl \rightleftharpoons R_2Si(OH)Cl.$$

can be an intermediate in the route of oligoorganosiloxane formation.

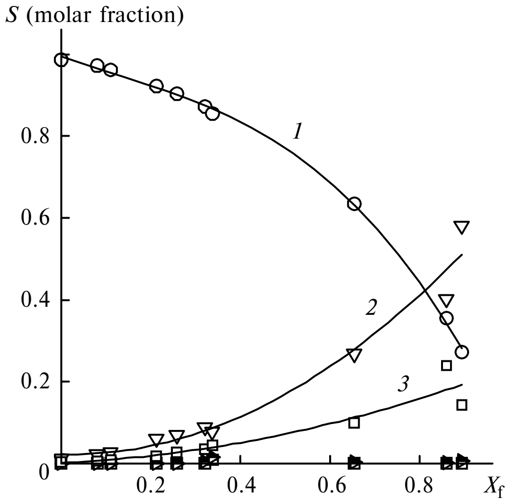


Fig. 7. Plots of the composition of the products (*S*) of the PH of $MePhSiCl_2$ in dioxane (60%) in the presence of the HCl acceptor (epichlorohydrin) *vs.* degree of conversion of functional groups (X_f): $MePhSiCl_2$ (*1*), $[MePhSiO]_3$ (*2*), and $[MePhSiO]_4$ (*3*).

However, the role of diorganosilanone as an intermediate in the synthesis of polyorganosiloxanes is not confirmed by other experiments[7,8] on the partial hydrolysis of Me_2SiCl_2 or 1,3-dichlorotetramethyldisiloxane in a medium of hexamethyldisiloxane, being a chemical trap for $R_2Si=O$. The hydrolysis of Me_2SiCl_2 was carried out in a well-stirred reactor at 20 °C and ratios of the reactants $Me_2SiCl_2 : Me_3SiOSiMe_3 = 1 : 1$ and $H_2O : Me_2SiCl_2 = 1 : 10—1 : 1$.

The reaction of hexamethyldisiloxane with silanone $Me_2Si=O$ formed during the hydrolysis of Me_2SiCl_2 should immediately afford insertion products, *i.e.*, $Me_3SiO(SiMe_2O)_nSiMe_3$. In fact, we found these products, not immediately after mixing of the reactants but after a long time (several min and h). Their amount increases on storage of the reaction mixture (Table 1).

Table 1. Composition of the hydrolysis products of dimethylchlorosilane (*A*) and 1,3-dichlorotetramethyldisiloxane (*B*) in hexamethyldisiloxane at the reactant ratio $Me_3SiOSiMe_3 : Me_2SiCl_2 : H_2O = 1 : 1 : 0.5$

Product	*n*	Content (mol.%)			
		A		*B*	
		I*	II**	I*	II**
$Cl(SiMe_2O)_{n-1}SiMe_2Cl$	1	23.1	0.0	0.0	0.0
	2	1.9	0.0	5.6	0.0
	3	0.0	0.0	0.0	0.0
	4	0.0	0.0	0.0	0.0
	5	0.0	0.0	0.0	0.0
	6	0.0	0.0	0.0	0.0
	7	0.0	0.0	0.0	0.0
	8	0.0	0.0	0.0	1.3
$Me_3SiO(SiMe_2O)_nSiMe_3$	0	64.4	30.4	59.3	23.8
	1	0.9	26.7	0.0	23.6
	2	0.8	16.3	2.3	16.2
	3	0.4	8.7	0.8	10.1
	4	0.2	3.4	0.5	7.6
	5	0.0	1.7	0.3	5.0
	6	0.0	0.6	0.0	3.9
	7	0.0	0.0	0.0	0.9
$(Me_2{'}SiO)_n$	3	4.2	2.9	6.6	0.0
	4	2.4	5.0	17.0	3.3
	5	0.8	2.6	3.9	1.3
	6	0.4	0.6	1.5	0.2
	7	0.0	0.0	0.5	0.0
	8	0.0	0.0	0.0	0.0
	9	0.0	0.0	0.0	2.1
	10	0.0	0.0	0.0	0.5

* After 1 h.

** After 4 days.

It is important to note that the composition of the hydrolysis products of 1,3-dichlorotetramethyldisiloxane containing no geminal chlorosilyl groups in a medium of hexamethyldisiloxane turned out (within the experimental error) to be the same as that in the case of Me_2SiCl_2. Identity of the compositions of the reaction mixtures after the hydrolysis of both indicated monomers was observed 1 h and 4 days after mixing of the reactants (see Table 1).

This fact indicates the formation of $Me_3SiO(SiMe_2O)_nSiMe_3$ during the catalytic rearrangement of hexamethyldisiloxane with the hydrolysis products of Me_2SiCl_2 and 1,3-dichlorotetramethyldisiloxane under the action of HCl. Therefore, assembling of the polymeric chain does not occur by the successive "insertion" of dimethylsilanone into molecules of hexamethyldisiloxane and bis(trimethylsiloxy)dimethylsiloxanes that formed. It was also established that the PHC of Me_2SiCl_2 in a medium of $(Me_2SiO)_m$ did not increase the ring size but increases the amount of cyclosiloxanes. These facts show that the application of chemical traps for diorganosilanone in the liquid phase ignoring the kinetic factors is not a reliable tool for its detection.

The performed analysis of published data and, in particular, comparison of the plots of the monomer conversion *vs.* degree of conversion of functional groups in HMFC processes, on the one hand, and HTFC and PHC, on the other hand, suggest that organochlorohydroxysilanes $R_nSiCl_m(OH)_{4-n-m}$ act as key intermediates, with the highest probability, in HPC under the studied experimental conditions. The heterofunctional condensation of these intermediates with each other and with the initial organochlorosilanes is the main way for chemical assembling of oligoorganosiloxanes. It cannot be ruled out that, under certain conditions, organochlorohydroxysilanes can be transformed into oligoorganosiloxanes through the stages of organosilanone formation followed by their polymerization but convincing proofs for this mechanism of chemical assembling of oligoorganosiloxanes during the HPC of organochlorosilanes have not yet been obtained.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 00-03-32843).

References

1. R. F. McCusker, *J. Am. Chem. Soc.*, 1953, **75**, 1585.
2. T. V. Vasil´eva, V. Ya. Stolyarenko, G. N. Yakovleva, and V. V. Yastrebov, *Zh. Obshch. Khim.*, 1982, **52**, 2570 [*J. Gen. Chem. USSR*, 1982, **52** (Engl. Transl.)]; K. Ruhlman, H. Grosse-Ruyken, and D. Scheller, *J. Organomet. Chem.*, 1988, **356**, 39.
3. P. V. Ivanov, V. I. Maslova, N. M. Buzyreva, N. G. Mazhorova, D. N. Golubykh, L. V. Kostikova, A. S. Mozzhukhin, and E. A. Chernyshev, *Zh. Vsesoyuzn. Khim. o-va im. D. I. Mendeleeva*, 1998, **42**, No. 6, 87 [*Mendeleev Chem. J.*, 1998, **42**, No. 6 (Engl. Transl.)].
4. P. V. Ivanov, Doct. Sci. (Chem.) Thesis, Moscow State Academy of Fine Chemical Technology, Moscow, 1998, 317 pp. (in Russian).
5. K. A. Andrianov and N. N. Sokolov, *Dokl. Akad. Nauk SSSR*, 1952, **82**, 909 [*Dokl. Chem.*, 1952 (Engl. Transl.)].
6. M. G. Voronkov, S. V. Basenko, and E. I. Dubinskaya, *Tez. Dokl. Vseros. Konf. "Kremniiorganicheskie soedineniya: sintez, svoistva, primenenie"* [*Organosilicon Compounds: Synthesis, Properties, Application*] *(Moscow, April 1—4, 2000)*, Moscow, 2000, L-2; S-66; S-68 (in Russian).
7. P. V. Ivanov and E. A. Chernyshev, in *Osnovnye dostizheniya nauchnykh shkol* [*Main Achievements of Scientific Schools*], IPTs MITKhT, Moscow, 2000, 207 (in Russian).
8. P. V. Ivanov, D. N. Golubykh, V. A. Pogodin, and E. A. Chernyshev, *Informatsionno-analiticheskii byulleten´ "Uchenye zapiski MITKhT"* [*Information Analytical Bulletin "Scientific Proceedings of Moscow State Academy of Fine Chemical Technology*], Izd-vo MITKhT im. M. V. Lomonosova, Moscow, 2000, No. 3, 13.
9. J. H. Cameron, T. A. Kleinhenz, and M. C. Hawley, *J. Ind. Chem. Fundam.*, 1975, **14**, 328.
10. L. H. Shaffer and E. M. Flanigen, *J. Phys. Chem.*, 1957, **61**, 1595.
11. V. P. Mileshkevich, G. A. Nikolaev, V. F. Evdokimov, and A. V. Karlin, *Zh. Obshch. Khim.*, 1971, **41**, 634 [*J. Gen. Chem. USSR*, 1971, **41** (Engl. Transl.)].
12. W. C. Shumb and A. J. Stevens, *J. Am. Chem. Soc.*, 1950, **72**, 3178.
13. B. N. Dolgov and Yu. A. Vol´nov, *Zh. Obshch. Khim.*, 1931, **1**, 91 [*J. Gen. Chem. USSR*, 1931, **1** (Engl. Transl.)].
14. H. S. Pink and F. S. Kipping *J. Chem. Soc.*, 1923, **123**, 2830; R. Robison and F. S. Kipping, *J. Chem. Soc.*, 1912, **101**, 2142.
15. M. F. Shostakovskii, Kh. I. Kondrat´ev, and V. I. Belyaev, *Dokl. Akad. Nauk SSSR*, 1955, **100**, 287 [*Dokl. Chem.*, 1955 (Engl. Transl.)].
16. Z. Lasocki and S. Chrzczonowicz, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 1961, **9**, 589.
17. W. T. Grubb and R. Osthoff, *J. Am. Chem. Soc.*, 1953, **75**, 2230.
18. N. N. Sokolov, in *Metody sinteza poliorganosiloksanov* [*Methods for Synthesis of Polyorganosiloxanes*], Gosenergoizdat, Moscow—Leningrad, 1959, p. 42 (in Russian).
19. Z. Lasocki, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 1964, **12**, 223.
20. N. I. Martyakova, S. B. Dolgoplosk, E. G. Kagan, and V. P. Mileshkevich, *Vysokomol. Soedin.*, *Ser. B*, 1971, **13**, 579 [*Polym. Sci. USSR*, *B*, 1971, **13** (Engl. Transl.)].
21. W. Rutz, D. Lange, H. Kelling, and E. Popowski, *Z. Anorg. Allg. Chem.*, 1986, **536**, 197.
22. P. V. Ivanov, N. I. Gel´perin, and V. V. Kireev, *Vysokomol. Soedin.*, *Ser. A*, 1985, **27**, 1041 [*Polym. Sci. USSR*, *A*, 1985, **27** (Engl. Transl.)].
23. G. N. Turkel´taub, P. V. Ivanov, A. G. Kuznetsova, N. A. Popova, and E. A. Chernyshev, *Vysokomol. Soedin., Ser. A*, 1998, **40**, 1 [*Polym. Sci.*, *A*, 1998, **40** (Engl. Transl.)].
24. P. V. Ivanov, V. I. Maslova, N. G. Bondareva, O. A. Yur´eva, N. V. Kozlova, E. A. Chernyshev, K. Yu. Odintsov, and E. A. Zykunova, *Izv. Akad. Nauk*, *Ser. Khim.*, 1997, 2256 [*Russ. Chem. Bull.*, 1997, **46**, No. 12 (Engl. Transl.)].
25. N. N. Sokolov, *Osnovy sinteza polimerov metodom polikondensatsii* [*Foundations of Synthesis of Polymers by the Polycondensation Method*], Khimiya, Moscow, 1979, 45 (in Russian).

26. V. M. Kopylov, L. M. Khananashvili, O. V. Shkol´nik, and A. G. Ivanov, *Vysokomol. Soedin.*, 1985, **37**, 394 [*Polym. Sci. USSR*, 1985, **37** (Engl. Transl.)].
27. V. V. Korol´ko, V. P. Mileshkevich, and V. I. Vecherskaya, *Tez. dokl. 1-go Vsesoyuz. simp. "Stroenie i reaktsionnaya sposobnost´ kremniiorganicheskikh soedinenii"* [*Abstrs. 1st All-Union Symp. "Structure and Reactivity of Organosilicon Compounds*] *(Irkutsk, September 27—30, 1977)*, IrIOKh, Irkutsk, 1977, 176 (in Russian).
28. R. C. Petersen and S. D. Ross, *J. Am. Chem. Soc.*, 1963, **85**, 3164.
29. D. Ya. Zhinkin, V. I. Ivanov, and V. I. Chernyak, *Zh. Obshch. Khim.*, 1982, **53**, 1320 [*J. Gen. Chem. USSR*, 1982, **53** (Engl. Transl.)].
30. A. G. Kuznetsova, K. A. Andrianov, and D. Ya. Zhinkin, *Plast. Massy* [*Plastics*], 1962, **6**, 19 (in Russian).
31. D. Ya. Zhinkin, G. N. Mal´nova, and A. P. Polonskaya, *Zh. Obshch. Khim.*, 1965, **35**, 1054 [*J. Gen. Chem. USSR*, 1965, **35** (Engl. Transl.)].
32. D. Petzelt and K. Ruhlmann, *Plaste Kautschuk*, 1979, **26**, 611.
33. P. V. Ivanov, N. I. Gel´perin, and V. V. Kireev, *Khim. Prom-st´* [*Chemical Industry*], 1986, No. 3, 142 (in Russian).
34. P. V. Ivanov and N. I. Gel´perin, *Khim. Prom-st´* [*Chemical Industry*], 1989, No. 4, 20 (in Russian).
35. I. V. Sakharova, V. A. Babicheva, and V. M. Kopylov, *Tez. dokl. 6-i Vsesoyuz. konf. "Khimiya i prakticheskoe primenenie kremniiorganicheskikh soedinenii"* [*Abstrs. 6th All-Union Conf. "Chemistry and Practical Application of Organosilicon Compounds*], Riga, 1986, 83; I. V. Sakharova, V. M. Kopylov, and L. M. Barakon´, Moscow, 1984, 27 pp. Dep. in VINITI, 758084 (in Russian).
36. Pat. 246766 GDR, 1987.
37. P. V. Ivanov, *Vysokomol. Soedin., Ser. A*, 1995, **37**, 417 [*Polym. Sci., A*, 1995, **37** (Engl. Transl.)].
38. N. N. Sokolov, in *Metody sinteza poliorganosiloksanov* [*Methods for Synthesis of Polyorganosiloxanes*], Gosenergoizdat, Moscow—Leningrad, 1959, p. 59 (in Russian).
39. K. A. Andrianov, S. A. Golubtsov, and N. N. Sokolov, *Vysokomol. Soedin.*, 1952, 1 [*Polym. Sci. USSR*, 1952 (Engl. Transl.)].
40. K. A. Andrianov, *Metody elementoorganicheskoi khimii* [*Methods of Organoelement Chemistry*], Nauka, Moscow, 1968, 699 pp. (in Russian).
41. G. Greber and L. Metzinger, *Makromol. Chem.*, 1960, **39**, No. 3, 167.
42. W. Patnode and D. Wilcok, *J. Am. Chem. Soc.,* 1946, **68**, 358.
43. W. H. Daudt and J. F. Hyde, *J. Am. Chem. Soc.,* 1952, **74**, 386.
44. V. N. Emel´yanov, Doct. Sci. (Chem.) Thesis, Institute of Synthetic Polymeric Materials, Moscow, 1988, p. 27 (in Russian).
45. M. V. Sobolevskii, L. M. Blekh, L. V. Sobolevskaya, G. A. Potashova, M. A. Kleinovskaya, and Yu. K. Molokanov, *Plast. Massy* [*Plastics*], 1976, **7**, 30 (in Russian).
46. M. G. Voronkov, *Zh. Obshch. Khim.*, 1998, **68**, 950 [*Russ. J. Gen. Chem.*, 1998, **68** (Engl. Transl.)].
47. D. N. Golubykh, V. A. Pogodin, and P. V. Ivanov, *Tez. dokl. Vseros. konf. "Kremniiorganicheskie soedineniya: sintez, svoistva, primenenie"* [*Abstrs. All-Russian Conf. Organosilicon Compounds: Synthesis, Properties, Applications*] *(Moscow, April 1—4, 2000)*, Moscow, 2000, S-154 (in Russian).
48. S. V. Basenko and M. G. Voronkov, *Dokl. Akad. Nauk*, 1994, **339**, 486 [*Dokl. Chem.*, 1994 (Engl. Transl.)].
49. M. G. Voronkov, *J. Organomet. Chem.*, 1998, **557**, 143.
50. M. G. Voronkov, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 824 [*Russ. Chem. Bull.*, 1998, **47**, 795 (Engl. Transl.)].
51. P. Lu, J. K. Paulasaari, and P. Weber, *Organometallics*, 1996, **15**, 4649.
52. L. E. Gusel´nikov and N. S. Nametkin, *Chem. Rev.*, 1979, **79**, 529; G. Raabe and J. Michl, *Chem. Rev.*, 1985, **85**, 420.
53. C. Le Roux, H. Yang, S. Wenzel, S. Grigoras, and M. Brook, *Organometallics,* 1998, **17**, 556.

Received February 6, 2001;
in revised form July 23, 2001