## Influence of macroscopic factors on the composition of the products of cohydrolysis of triorganochlorosilanes

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The composition of the products of heterogeneous cohydrolysis of trimethyl- and dimethylphenylchlorosilanes by excess aqueous ammonia (4--5% solution) is determined by the regime of heterofunctional condensation of the initial chlorosilanes with the products of their hydrolysis, triorganosilanols. In a diffusion regime, hexaorganodisiloxanes are formed because of the limited possibility of removing silanols from the reaction zone, while silanols are predominantly formed in a kinetic regime. The influence of the nature of the solvent and surfactant and the intensity of stirring of the reaction mixture on the composition of the final products of hydrolytic cocondensation of triorganochlorosilanes is considered.

Key words: hydrolytic cocondensation, triorganochlorosilanes, hexaorganodisiloxanes, hydrolysis, hetero- and homofunctional condensation; diffusion and kinetic regimes.

The most important methods for the preparation of polyorganosiloxanes (POS) and organocyclosiloxanes with different units on the industrial scale and in the laboratory are based on hydrolytic copolycondensation (HCP) of organochlorosilanes (OCS). The initial stages of this process are poorly known despite the great importance of HCP.

It is of special interest to study the initial stages of HCP, because the microstructure of the polymer is formed at these stages. The regularities of the formation of the reaction centers at the initial stages determine the composition, structure, yield, and polydispersity of the copolymer. The reaction centers can be formed and transformed under heterophase conditions when the processes are limited by mass transfer.<sup>1</sup> This should be taken into account for controlling the composition of the products of HCP.

In the present work, the regularities of HCP were studied using the model system of cohydrolysis of triorganochlorosilanes as an example.

## Experimental

Cohydrolysis of triorganochlorosilanes was performed in acetone, toluene, or without solvent by aqueous ammonia (4– 5% solution) at 20–30°C and using a stirrer with a rotation velocity of 100–2500 min<sup>-1</sup>. The process was carried out in a batch microreactor 1.2 cm in diameter with a stirrer and reflecting fins. An equimolar ratio of Me<sub>3</sub>SiCl and Me<sub>2</sub>PhSiCl, a 60% concentration of the solvent, and a total 30% concentration of R<sub>3</sub>SiCl in their mixtures with water (X) were used. The specified ratio of the reagents was achieved by fast (0.5 s) injection of a mixture of triorganochlorosilanes into an aqueous-organic solution of ammonia.

The relative composition of the products of cohydrolysis (in further discussion for shortness, "content" S, %) was determined by GLC (the method of normalization of the surface areas using correction coefficients; helium was used as carrier-gas, column  $3m \times 3mm$ , sorbents: Chromaton N-AW-DMCS with 5% SE-30 and 10% PMS-100, as well as Polysorb-1 with 5% polyethylene glycol-20000). The relative error of analysis was 5–12%.

## **Results and Discussion**

All three types of reactions studied: hydrolysis (1) and (2); homofunctional condensation (HMFC) (3)--(5); and heterofunctional condensation (HTFC) (6)--(9), occur via an  $S_N2$  mechanism and can be both reversible or irreversible. This scheme can be more complicated when exchange reactions between silanols and chlorosilanes are taken into account.<sup>2</sup>

$$R_3 SiCI + H_2 O \longrightarrow R_3 SiOH + HCI$$
(1)

$$R'_{3}SiCl + H_{2}O \longrightarrow R'_{3}SiOH + HCl$$
(2)

$$R_3 SiOH + R_3 SiOH --- R_3 SiOSiR_3 + H_2 O$$
(3)

$$R'_{3}SiOH + R'_{3}SiOH \longrightarrow R'_{3}SiOSiR'_{3} + H_{2}O$$
 (4)

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 $R_{3}SIOH + R'_{3}SIOH \longrightarrow R_{3}SIOSIR'_{3} + H_{2}O$ (5)

 $R_3SiCl + R_3SiOH \longrightarrow R_3SiOSiR_3 + HCl$  (6)

 $R'_{3}SiCl + R_{3}SiOH \longrightarrow R_{3}SiOSiR'_{3} + HCl$  (7)

 $R_3SiCI + R'_3SiOH \longrightarrow R_3SiOSiR'_3 + HCI$  (8)

 $R'_{3}SiCI + R'_{3}SiOH \longrightarrow R'_{3}SiOSiR'_{3} + HCI$ (9)

Thus, a siloxane bond can be formed in HMFC of the silanols obtained (3)-(5) and in their HTFC with the initial OCS. The regularities of these processes differ substantially. The possibility of the simultaneous occurrence of  $\equiv$ SiCl and  $\equiv$ SiOH reaction centers in the reaction mass and their ratio are determined by both kinetic and macrokinetic factors. Evidently, this ratio depends, first, on the ratio of the rate constants of hydrolysis, HMFC, and HTFC, and second, on the ratio of the concentrations of OCS and water in the reaction zone.

The majority of the available published data on the kinetics of hydrolysis<sup>3</sup> and HMFC<sup>4</sup> cannot be compared, because they occur under different conditions. The kinetics of HTFC has been studied only for the reactions of triorganochlorosilanes with dimethyl-carboranylsilanol<sup>5</sup> and the exchange reactions of OCS with silanols.<sup>2</sup>

Based on the general regularities of  $S_N 2$  substitution at the silicon atom, the reaction rate constants can be arranged in decreasing order: hydrolysis > HTFC > HMFC. The ratio of the rates of hydrolysis (1) and HTFC (6)-(9) can be approximately estimated from the ratio of the rate constants of hydrolysis (10) and alcoholysis (11) of chlorodiethoxyphenylsilane. The latter was calculated from the published<sup>6</sup> data and was equal to 1 : 0.05. This ratio can be greater, because the basicity of silanols (as nucleophiles) is lower than that of alcohols, and their steric factor is higher.

 $PhSi(OEt)_2CI + H_2O \longrightarrow PhSi(OEt)_2OH + HCI$  (10)

 $PhSi(OEt)_2Cl + EtOH \longrightarrow PhSi(OEt)_3 + HCl$  (11)

Calculations for consecutive-parallel reactions (1) and (6) based on the ratio of the rate constants at an equimolar ratio of water and organochlorosilane indicated that silanol must be the main product (>85%). Therefore, the common statement that organosiloxanes are formed in HMFC of silanols seems to be reasonable.

However, in the case of cohydrolysis of OCS, the degree of HTFC can be higher due to the different reactivities of the co-monomers: when the concentration of the less reactive OCS is greater at the moment of formation of the highly reactive silanol, the product of the concentrations  $[R'_3SiCI][R_3SiOH]$  increases, which results in a high rate of HTFC.

It is assumed in some works that a product of cocondensation (PCC) is formed in HTFC of the hydroxy derivative of a more reactive OCS with an OCS which is less prone to hydrolysis. In the cohydrolysis of methyldichlorosilane and diphenyldichlorosilane under the action of an equimolar amount of water, the replacement of diphenylchlorosilane with the product of its hydrolysis (diphenylsilanediol) resulted in a decrease in the number of phenylsiloxane units in cyclosiloxanes with different units.<sup>7</sup> This probably indicates that cyclosiloxanes with different units are formed in HTFC of MeHSi(OH)<sub>2</sub> with Ph<sub>2</sub>SiCl<sub>2</sub> rather than in HMFC of MeHSi(OH)<sub>2</sub> and Ph<sub>2</sub>Si(OH)<sub>2</sub>.

The data on cohydrolysis of phenyltrichlorosilane and diethyldichlorosilane by an insufficient amount of water made it possible to assume that oligoorganosiloxanes with different units are preferably formed in HTFC of hydroxyl derivatives of the more reactive phenyltrichlorosilane with the relatively less hydrolyzed diethyldichlorosilane.<sup>8</sup>

In fact, it can be assumed that the rates of HMFC (3)-(5) are considerably lower than those of HTFC (6)-(9) because, when the same nucleophile R<sub>3</sub>SiOH is involved in reactions (3) and (4), (6) and (8), and (7) and (9), triorganochlorosilanes R<sub>3</sub>SiCl and R'<sub>3</sub>SiCl are substrates with a "better" leaving group than the corresponding silanols in reactions (3)-(5).

The primary role of HTFC is also unambiguous due to the fact that in the case of hydrolysis of OCS by an insufficient amount of water (partial hydrolysis) the unconsumed OCS inevitably reacts with the silanol formed.

It could be expected that HMFC reactions (3)-(5)would be the main route of the formation of the  $\approx$ SiO-Si $\approx$  bond in the case of cohydrolysis of OCS by excess water, because, according to our estimation (see above), HTFC reactions are no more than 15% complete at the time hydrolysis reactions (1) and (2) are completed. However, the available experimental data show that in this case PCC are synthesized through the HTFC mechanism as well.

The study of cohydrolysis of trimethyl- and triethylchlorosilane by excess water in benzene made it possible to propose<sup>9</sup> that PCC (Me<sub>3</sub>SiOSiEt<sub>3</sub>) are formed at the interface due to the reaction of trimethylsilanol with triethylchlorosilane. Hexaethyldisiloxane is formed in the organic phase by HTFC in reaction (9). Hexamethyldisiloxane is formed in the aqueous phase due to HMFC in reaction (3). In general, these data agree with the results of Ref. 7, according to which the yield of organocyclosiloxanes with different units is higher when a solvent immiscible with water is used.

We have shown previously 10-13 that in the case of hydrolysis by excess water, HTFC is the main reaction of the formation of the siloxane bond even in the medium of a common solvent. However, there are no published data on the regularities and composition of the products of HCC of triorganochlorosilanes by excess water in a common solvent. In this work, the heterophase HCC of triorganochlorosilanes was studied in the diffusion and kinetic regimes.

We chose the relative content of triorganosilanols in the products of HCC of triorganochlorosilanes as the criterion for the boundary between the diffusion and kinetic zones of cohydrolysis. The validity of using this criterion has been analyzed in detail:<sup>12,13</sup> any heterogeneity in the distribution of the reagents in the bulk or at the phase interface results in the formation of zones with increased concentrations of R<sub>3</sub>SiOH and R<sub>3</sub>SiCl. This inevitably results in their reaction via the HTFC mechanism and, as a consequence, in a decrease in the content of R<sub>3</sub>SiOH.

Cohydrolysis in organic solvents. As has been shown previously,<sup>10,11</sup> in the case of a common solvent, the hydrolysis of OCS in the kinetic regime occurs simultaneously in the organic and aqueous phases of the system. Both in the presence<sup>10</sup> and absence<sup>14</sup> of an acceptor of HCl, organosiloxanes are predominantly formed through HTFC. In addition, it is established that ammonia has no effect (within the experimental error) on the phase distribution of the components of the reaction system. This is confirmed by the fact that the regions of conode lines of the phase quasi-equilibrium (at  $X \le 50$ ) coincide in the presence and absence of ammonia.14 However, the compositions of the products of hydrolysis of diorganodichlorosilanes at pH 7-8 and pH < 1 differ considerably due to the contribution of HMTC to the formation of oligosiloxanes. Therefore, aqueous ammonia was used as the acceptor of HCI (to suppress HMFC) to determine the degree of HTFC in the cohydrolysis of organochlorosilanes. The experimental data presented below are discussed from the viewpoint of the influence of the reaction conditions on the degree of HTFC.

Our experiments (Fig. 1, a) showed that in acetone the content of Me<sub>3</sub>SiOH and Me<sub>3</sub>PhSiOH first increases as the circular flow rate (v) increases and then becomes constant at v > 1 m s<sup>-1</sup>. When the v values are low, the reaction system is characterized by a poorly developed surface of phase contact and a nonuniform distribution of the components in the bulk. As a result, under these conditions, HCC of Me<sub>3</sub>SiCl and Me<sub>2</sub>PhSiCl is limited by both the velocity of the supply of reagents to the reaction zone and the velocity of the removal of the Me<sub>3</sub>SiOH and Me<sub>2</sub>PhSiOH formed from the reaction zone. The area of the interphase surface and the intensity of heat exchange increase as v increases. At v > $1 \text{ m s}^{-1}$ , independence of the content of the reagents is achieved, which corresponds to a kinetic regime of the process.

As can be seen in Fig. 1, a, the main products of cohydrolysis are silanols, which are probably formed in the bulk of the phases that has not been completely formed (quasi-equilibrium phases).

It is of interest that when  $v \le 1.2 \text{ m s}^{-1}$ , the content of Me<sub>3</sub>SiOH is lower than that of Me<sub>2</sub>PhSiOH. This is explained by the fact that since Me<sub>3</sub>SiOH is a more



Fig. 1. Dependence of the relative content (S) of products of cohydrolysis of Me<sub>3</sub>SiCl and Me<sub>2</sub>PhSiCl on the stirring rate (v) in acetone (a), toluene and toluene+surfactant (dotted line) (b), and without solvent (c): Me<sub>3</sub>SiOH (1), Me<sub>3</sub>SiOSiMe<sub>3</sub> (2), Me<sub>2</sub>PhSiOH (3), Me<sub>2</sub>PhSiOSiPhMe<sub>2</sub> (4), and Me<sub>3</sub>SiOSiPhMe<sub>2</sub> (5).

|                    |  |  | - |
|--------------------|--|--|---|
| R <sub>3</sub> SiX | Equilibrium concentrations             |  |   |
|                    | H <sub>2</sub> O in R <sub>3</sub> SiX | R <sub>3</sub> SiX in H <sub>2</sub> O |   |
| MeiSiCl            | 0.41                                   | 0.85 · 10 <sup>-2</sup>                |   |
| MenPhSiCl          | 0.52                                   | 0.78 + 10-4                            |   |

**Table 1.** Equilibrium concentrations (mol.%) of water,  $R_3SiCI$ , and  $R_3SiOH$  in binary  $H_3O-R_3SiX$  mixtures at 20 °C

0.15

 $0.23 \cdot 10^{-2}$ 

Note. R<sub>3</sub>SiX and R<sub>3</sub>SiOH are miscible in all ratios.

36.4

22.4

Me<sub>3</sub>SiOH

Me<sub>1</sub>PhSiOH

reactive silanol, it is consumed to a greater extent in the HTFC reactions with Me<sub>3</sub>SiCl and Me<sub>2</sub>PhSiCl to give Me<sub>3</sub>SiOSiMe<sub>3</sub>, and Me<sub>3</sub>SiOSiPhMe<sub>2</sub> is formed as PCC. If  $v > 1.2 \text{ m s}^{-1}$  when the process becomes heterophase, the contents of Me<sub>3</sub>SiOH and Me<sub>2</sub>PhSiOH become equal (see Fig. 1, *a*).

As the preliminary UNIFAC calculations of the phase quasi-equilibrium of the acetone-water-Me<sub>3</sub>SiCl and Me<sub>2</sub>PhSiCl systems showed,<sup>15</sup> the fact that the yields of the two silanols are equal can be explained by the considerably better solubility of Me<sub>3</sub>SiOH in the aqueous phase than Me<sub>2</sub>PhSiOH (Table 1). Therefore, a portion of Me<sub>3</sub>SiOH is retained in the aqueous phase, which compensates for its consumption in HTFC in the organic phase.

When  $v > 1.2 \text{ m s}^{-1}$ , the total yield of Me<sub>3</sub>SiOH and Me<sub>2</sub>PhSiOH reaches ~70% (Fig. 2, *a*). When Me<sub>3</sub>SiOH and Me<sub>2</sub>PhSiOH are hydrolyzed separately, their content is equal to 85–90%.<sup>12</sup> This difference is explained by the fact that, unlike hydrolysis of OCS, in cohydrolysis four HTFC reactions (6)–(9) occur.

The quantitative composition of the HCC products in toluene, which is immiscible with water, (Fig. 1, b) differs substantially from that considered above: (1) although the composition of the products approaches a constant value, it does not reach it at  $v \ge 1.6$  m s<sup>-1</sup>, which indicates that the reactions occur near the interface in a diffusion (or intermediate) regime; (2) the total yield of  $R_3$ SiOH in toluene is lower than in acetone (see Fig. 2, a), which indicates the resistance of the transfer of silanols to the aqueous phase in the absence of acetone due to their low solubility in water (see Table 1). For this reason, the degree of interaction of the more reactive Me<sub>3</sub>SiOH with the initial OCS is higher than in the acetone-water system. Therefore, the degree of participation of Me<sub>2</sub>PhSiOH in HTFC reactions is lower and its yield is higher.

Effect of surfactant on the composition of the cohydrolysis product. Since the hydrolysis of organochlorosilanes is heterogeneous, it was of interest to study the effect of surfactants on the composition of the products of cohydrolysis of Me<sub>3</sub>SiCl and Me<sub>2</sub>PhSiCl. It is known that surfactants in heterogeneous systems result in several phenomena:<sup>16</sup> (1) since they occupy a part of the surface, adsorbed layers of a surfactant are a barrier to mass transfer; (2) surfactants decrease the size of the globules of the dispersion phase and, as a consequence,





Fig. 2. Dependence of the relative total content (S) of Me<sub>3</sub>SiOH and Me<sub>2</sub>PhSiOH (a) and Me<sub>3</sub>SiOSiPhMe<sub>2</sub> (b) on the stirring rate (v): acetone (l), toluene (2), toluene+surfactant (3), and without solvent (4).

increase the area of the interface, which intensifies the mass transfer.

According to the data in Ref. 17, the second effect is stronger, as a rule, than the first one. The data in Ref. 18 show that the two effects compensate for each other. It is also considered that when the time of phase contact is small, *i.e.*, in systems with vigorous stirring, surfactant molecules do not diffuse to the interface and, hence, their effect is small or is completely absent.<sup>16</sup>

The results of our experiments showed (see Fig. 1, b) that when the intensity of stirring of the components is low (less than  $0.3 \text{ m s}^{-1}$ ), the total yield of silanols

decreases in the presence of surfactants (see Fig. 2, *a*) and the yield of PCC increases (see Fig. 2, *b*). Probably, under these conditions, the effect of shielding of the interface by surfactants molecules prevails. Due to this, the removal of  $R_3SiOH$  molecules into the aqueous phase is retarded and, as a consequence, the degree of HTFC increases. The degree of HTFC in the presence of the surfactant at v < 0.3 m s<sup>-1</sup> can also increase due to another surfactant effect: a decrease in the internal circulation of the liquid within globules of the dispersion phase.

It also can be seen in Figs. 1, b and 2, b that the slope of the function of the content of PCC (S) vs. v is greater in the presence of a surfactant. This is caused by the second effect of the surfactant: a decrease in the phase tension, which facilitates a faster increase in the surface of the interface and, hence, an increase in the part of the surface free from the surfactant for transferring components. This results (at  $v > 0.3 \text{ m s}^{-1}$ ) in an increase in the content of silanols over that of a system without a surfactant (see Fig. 2, a). Finally, when  $v > 1.4 \text{ m s}^{-1}$ , the contents of all cohydrolysis products become equal in both systems considered (see Fig. 1, b) because the effect of the surfactant is significant.

Thus, there are three intervals of change in v corresponding to 1) the predomination of the retardation of mass transfer of the components in the reaction system (less than 0.3 m s<sup>-1</sup>), 2) its acceleration (0.3–1.5 m s<sup>-1</sup>), and 3) the absence of a surfactant effect (>1.4 m s<sup>-1</sup>). The differences detected in the composition of the cohydrolysis products are not very great and sometimes are within the experimental error.

Cohydrolysis in the absence of solvent. The regularities of the cohydrolysis of  $R_3SiCl$  in toluene and acetone differ substantially from those in the absence of a solvent. For example, the cohydrolysis of  $Me_3SiCl$  and  $Me_2PhSiCl$  without a solvent results in a sharp change in the composition of the products. The main product is PCC, and its content decreases insignificantly as v increases (see Fig. 1, c, 2, b). Under these conditions, the yield of  $R_3SiOH$  is several times lower than that in the toluene—water system.

Since the aqueous phases of the systems compared are almost the same (a 4-5% solution of ammonia), one must search for the reasons for the high intensity of HTFC in the differences between the organic phases or the interfaces.

By analogy with the two consecutive first-order reactions analyzed in Ref. 19, let us consider the heterogeneous hydrolysis of  $R_3SiCI$  followed by HTFC as a model:

$$X + W \xrightarrow{k_1} S + A,$$
$$X + S \xrightarrow{k_2} D + A,$$

where X is  $R_3SiCI$ , W is  $H_2O$ , S is  $R_3SiOH$ , D is  $R_3SiOSiR_3$ , and A is HCl.

For the quasi-stationary state (*i.e.*, when the diffusion flows (J) and the rates of the chemical stages (r) are equal), assuming that the reactions are irreversible, the following equations can be written:

$$J_{W} = \beta_{W}(C_{W}^{v} - C_{W}) = r_{W} = k_{1}C_{X}C_{W}, \qquad (12)$$

$$J_{X} = \beta_{X}(C_{X}^{\vee} - C_{X}) = r_{X} = k_{1}C_{X}C_{W} + k_{2}C_{X}C_{S}, \quad (13)$$

where the upper indices "v" designate the concentrations of the components in the bulk; the absence of an index designates the concentration at the interface; and the lower indices designate the substances X, W, and S, *i.e.*,  $R_3SiCl$ ,  $H_2O$ , and  $R_3SiOH$ , respectively;  $\beta_W$  and  $\beta_X$  are the mass-transfer coefficients;  $k_1$  and  $k_2$  are the rate constants of the stages.

The ratio of the products of the hydrolytic cocondensation of  $R_3SiOH$  and  $R_3SiOSiR_3$  is equal to the ratio of the rates of their formation:

$$\frac{r_{\rm S}}{r_{\rm D}} = \frac{k_1}{k_2} \cdot \frac{C_{\rm W}}{C_{\rm S}} - 1 \quad . \tag{14}$$

It follows from Eq. (14) that the predominant formation of  $R_3SiOH$  requires that  $k_1 >> k_2$  and that the concentration  $C_S$  in the reaction zone be minimal. The  $C_S$  concentration can be decreased by intensification of stirring, dilution of the reaction system with a solvent, and removal of  $R_3SiOH$  from the reaction zone (for example, by extraction to a nonreaction phase).

The experimental  $C_S$  concentration is unknown. Therefore, let us determine its value from the condition of quasi-stationarity of process (12). In the case of two consecutive first-order reactions, the situation in which the concentration of the intermediate product in the bulk (in our case,  $R_3SiOH$ ) is equal to zero:  $C_S^v = 0$  has been considered.<sup>19</sup> In fact, this condition means that the reaction of formation of S occurs instantly. Then the solution of Eq. (14) relative to the desired  $C_S$  concentration is the following:

$$C_{\rm S} = \frac{k_1 C_{\rm X} C_{\rm W}}{\beta_{\rm S} + k_2 C_{\rm X}} \quad . \tag{15}$$

Substituting this value into Eq. (14), we obtain:

$$\frac{J_{\rm S}}{J_{\rm D}} = \frac{\beta_{\rm S}}{k_2} \cdot \frac{1}{C_{\rm X}} \tag{16}$$

Evidently, the greater the concentration of R<sub>3</sub>SiCl in the organic phase  $(C_X^v)$ , the greater its concentration at the interface  $(C_X)$ . Therefore, the difference in the compositions of the cohydrolysis products Me<sub>3</sub>SiCl and Me<sub>2</sub>PhSiCl in the acetone—water—chlorosilane, toluene—water—chlorosilane, and water—chlorosilane systems can be explained by Eq. (16). In the three systems considered, the  $C_X^v$  concentrations increase in the following order: 1.1, 1.5, and 7.1 mol L<sup>-1</sup>.\* In the latter

<sup>\*</sup> Calculated by the UNIFAC method.

case,  $R_3SiCl$  is not diluted with a solvent, and  $C_X$  takes it maximum value. According to Eq. (16), the total content of silanols in this system is minimum (see Fig. 2, *a*). A comparison of the content of PCC (Me<sub>3</sub>SiOSiPhMe<sub>2</sub>, Fig. 2, *b*) shows that it increases as the initial concentration increases.

An important conclusion can be drawn from Eq. (16): the composition of HCC products is determined by the regime in which HTFC proceeds. If  $\beta_S >> k_2$ , HTFC occurs in a kinetic regime, and the R<sub>3</sub>SiOH formed is removed from the reaction zone to the aqueous phase and becomes the main product of the process. If HTFC occurs in a diffusion regime ( $\beta_S << k_2$ ), R<sub>3</sub>SiOH is transformed into R<sub>3</sub>SiOSiR<sub>3</sub> more rapidly than it is removed from the reaction zone.

It follows from the aforesaid that the content of the intermediate products ( $R_3$ SiOH) is a criterion of the regime of HTFC. Therefore, the regions of the conode lines of the phase quasi-equilibrium of the organo-chlorosilane-water-solvent systems obtained previously<sup>11,12,14</sup> characterize the phase quasi-equilibrium of the reaction system that preceded the HTFC reactions.

It is noteworthy that Eq. (16) was derived without taking into account the concentration profile of the reagents at the interface and their partition coefficients. This equation reflects only the general ratio of kinetic and diffusion factors. For a more exact analysis of the process and determination of the  $C_X$  values, the reactions should be considered in both the organic and aqueous phases. However, this is outside the scope of the present work.

According to the published data,<sup>20</sup> the hydrolysis even of 3-chloroheptamethyltrisiloxane in the toluene--water system occurs in the diffusion region. This confirms that the boundary condition  $C_{\rm S}^{\rm v} = 0$  was chosen correctly. Taking into account that the rate constants of the hydrolysis of commonly used OCS (for R<sub>3</sub>SiCl, 10<sup>-3</sup>--0.5;<sup>21</sup>; for R<sub>2</sub>SiCl<sub>2</sub>, 10<sup>-2</sup>--2;<sup>22</sup> and for RSiCl<sub>3</sub>, >4 <sup>22</sup>) are greater than the boundary Hatta value (~4 · 10<sup>-3</sup> s<sup>-1</sup>),<sup>23</sup> cousidered to the heterogeneous hydrolysis of the majority of OCS can be occur in the diffusion region.

The degree and regime of HTFC depend on the functionality and reactivity of organochlorosilane. Taking into account that the rate constants of HTFC can be 10-100 times lower than the rate constants of hydrolysis of organochlorosilanes, it should be expected that HTFC can occur in both the kinetic and diffusion regimes. This makes studying HCC of OCS considerably more difficult.

Since a deficiency of water in the reaction zone is one of the reasons for intense HTFC,<sup>1</sup> the partial cohydrolysis of Me<sub>3</sub>SiCl and Me<sub>2</sub>PhSiCl in the absence of an acceptor of HCl was performed to model the cohydrolysis in the bulk of the organic phase. The average relative content of PCC in the totality of  $(R_3Si)_2O$ obtained was equal to 35-47%, *i.e.*, it was the same as those in the three systems considered with an acceptor of HCl (38-42%). In addition, the content of PCC in  $(R_3Si)_2O$  is almost independent of the intensity of stirring, which suggests that they are formed in the bulk of the organic phase, *i.e.*, under homogeneous conditions when diffusion retardation is significant at values of rate constants of ~10<sup>7</sup> L mol<sup>-1</sup> s<sup>-1</sup>.<sup>24</sup>

In the case when PCC ( $Me_3SiOSiPhMe_2$ ) is obtained only in HTFC (5), its content would not exceed 30% when reactivity of the reagents is equal.<sup>25</sup> The high content of PCC in our and other experiments<sup>9</sup> is explained by its simultaneous formation in two HTFC reactions ((7) and (8)).

Thus, the products of HCC of triorganochlorosilanes both in the presence and absence of an acceptor of HCl are predominantly obtained through HTFC. The experimental and published data presented show that in HCC of OCS in solvents miscible and immiscible with water, the siloxane bond is predominantly formed in the reaction of HTFC of the hydrolysis products with the initial OCS. The reason for the intense HTFC in the hydrolysis of OCS by excess water in the medium of a common solvent is the heterophase character of the process, which causes a deficiency of the hydrolyzing reagent in the organic phase or limitation of the process by mass transfer.

The composition of the products of HCC and hydrolysis of OCS is determined by the regime of HTFC: when v > 1.6 m s<sup>-1</sup>, the composition of the products of HCC of OCS corresponds to a process limited by the HTFC rate only in the medium of a common solvent. In the medium of solvents immiscible with water or in their absence, HTFC occurs in the intermediate or diffusion regime. The main resistance to mass transfer is concentrated at the interface.

It can be assumed that the interval of HTFC rates of different OCS is the boundary between the rates of purely diffusion (hydrolysis of chlorosilanes) and kinetic (HMFC of silanols) reactions. This situation should be specially monitored in technological processes.

An important practical conclusion follows from the results of the work: the hydrolysis of OCS by excess water is unreasonable. In addition, it is accompanied by the formation of a great amount of hydrochloric waste. That is the reason why the tendency to decrease the amount of hydrolyzing agent has been observed recently.<sup>26</sup>

Thus, the preparation of polyorganosiloxanes of different compositions and structures by hydrolysis of OCS accompanied by the formation of HCl should be performed using a hydrolyzing agent in amounts not greater than those required for the achievement of the desired molecular weight and structure.

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