The role of the phase quasiequilibrium in the reaction system chlorotriorganosilane—water—acetone

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On the basis of analysis of product composition in the hydrolytic polycondensation (HPC) of chlorotriorganosilanes, the parameters of the kinetic and the diffusion field, the zone of the reaction, and the region of the conodes of the phase diagrams are determined. It is suggested that the conodes correspond to a phase quasiequilibrium, which defines the composition of the reaction products. The results of this investigation confirm the previously discovered features of HPC of dichloromethylphenylsilanes: the formation of the siloxane bond during the hydrolysis of chloroorganosilanes by water mainly occurs in the organic phase of the system and proceeds as the heterofunctional polycondensation of the reaction products with the starting chloroorganosilanes. The role of the phase quasiequilibrium consists of the creation of a field of reagent concentration, based on which one can control the composition of the reaction products.

Key words: phase quasiequilibrium; conodes; Gibbs phase diagram; hydrolysis; chloroorganosilanes; silanols; field of the reaction.

The role of the phase state of reaction systems in the control of chemical processes and in the creation of new synthetic methods is one of the current chemical problems. Evaluation of the influence of the phase state of reaction systems is a subject of investigations in the fields of polymer synthesis,^{1,2} phase-transfer catalysis,³ heterogeneous organic reactions,⁴ and other processes of mass-exchange during a reaction.⁵ The main role of mass-exchange in these processes is the creation of a field of concentrated reagents, which is necessary in order for them to interact in the proper ratio, and also for the withdrawal of target or side products from the reaction zone. We have found¹ that the synthesis of organosilanoles is complicated not by their condensation at the hydroxyl groups, as is generally believed:

$$R_3 SiCl + nH_2 O \rightarrow R_3 SiOH + HCl + (n-1)H_2 O; n \gg 1, \quad (1)$$

$$2R_3SiOH \rightarrow (R_3Si)_2O + H_2O, \qquad (2)$$

but ruther by heterofunctional polycondensation (HFPC) with the initial chlorosilane:

$$R_3 SiOH + R_3 SiCl \rightarrow (R_3 Si)_2 O + HCl.$$
(3)

Unlike the above mentioned heterophasic processes, the initial stages of hydrolytic polycondensation (HPC) of chloroorganosilanes are two-phase, not due to the use of solvents that are finitely miscible, but because water and chlorosilane are at the same time both the reagents and the phase-forming (partially mutually soluble) components. Therefore, the initial reaction mixture divides into organic and aqueous phases. In both phases silanol is formed, which reacts in the organic phase with the unchanged chlorosilane due to the deficiency of water to give siloxane. Thus, the yield of silanol depends on the volume ratio of the phases, as has been shown for the hydrolysis of dichloromethylphenylsilane.¹

In the literature, methods for the simultaneous investigation of heterophase systems and chemical and phase equilibria have been described, 5-7 attempts to analyze systems on the basis of a study of the phase equilibrium in the absence of one of the reagents have been reported, and inhibitors, luminescent and radioactive labels, mass-molecular distribution,⁸ etc.² have been suggested.

The method that we have elaborated for the investigation of phase quasiequilibrium is based on the realization of a reactive mass-exchange process in a kinetic field and also on the determination of the conodes (the chords of phase equilibria) and the phase compositions using the composition of the products formed in these phases. 1,9,10

Since the composition of the reaction system is changing from the moment when the components are mixed and the chemical reactions start until the end of these reactions, the phase state of the system is also dynamic. Under conditions in which the process is limited by the chemical interactions, the reaction system goes through many quasiequilibrium states. The question of which of the phase quasiequilibria is character-

Translated from Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 7, pp. 1222–1226, July, 1994. 1066-5285/94/4307-1156 \$12.50 © 1995 Plenum Publishing Corporation ized by the obtained experimental data is very complicated. For example, in the case of the hydrolysis of dichloromethylphenylsilane, it is not yet clear, with which of the phase quasiequilibria the obtained portions of the conodes are associated, *i.e.*, with the initial equilibrium (dichloromethylphenylsilane-water-acetone), with the intermediate equilibrium (after hydrolytic cleavage of the first chlorine atom), or with the state when the water is completely consumed in the organic phase. It is also unclear whether redistribution of the components occurs after each of the chemical interactions, or the hydrolytic reactions in the phases proceed as if in closed microreactors.

The purpose of this work is to investigate the effect of the phase state of the reaction system on the composition of the products of hydrolysis of chlorotriorganosilanes and to determine the boundaries of the kinetic and the diffusion field of the process and the conode lines of phase quasiequilibrium.

Experimental

Hydrolysis of chlorotrimethylsilane (1) was carried out in a tubular direct-flow reactor with an injector installed at the entrance port as a mixer, in which chlorosilane, acetone, and ammonia (as an aqueous solution)¹ were simultaneously introduced by dosing pumps to minimize homofunctional condensation of the silanols obtained. The time of mixing in the injector was 0.03-0.10 s, the contact time of the reaction mixture in the reactor was 10-15 s, and pH was 7.5. The conditions described allow the preset composition to be maintained for the required time interval and the products to be removed from the reaction zone.

To determine the boundaries of the kinetic and the diffusion field of hydrolysis of 1, chlorodimethylphenylsilane (2), and chloromethyldiphenylsilane (3), the process was also carried out in a reactor with a spherical bottom and in a reactor with a flat bottom and reflecting partitions. There was a mixer in both reactors.

The selectivity of hydrolysis with respect to trimethylsilanol (1a) and dimethylphenylsilanol (2a) was monitored by GLC (LKhM-80; carrier gas helium; column 3 m \times 3 mm; sorbent Chromaton N-AW-DMCS with 5 % SE-30 and 10 % PMS-100), and the selectivity of the hydrolysis with respect to methyldiphenylsilanol (3a) was determined by quantitative TLC (Dual-wavelength Flying-spot Scanner CS-9000; Silufol-UV 254, 30 \times 130 mm; toluene—acetonitril, 15 : 1).

The relative content of acetone in the reaction mixture (A) and the content of chlorosilane in its mixture with water (X) were the variable parameters of the process. Similar to the method of titration of a binary mixture with a third component, which is used for determination of a binodal curve,⁶ the hydrolysis was carried out so that the composition of the products of HPC was determined for the constant X at various A by quantitative TLC and GC methods.

Results and Discussion

It is generally believed that hydrolysis of chlorotriorganosilanes is a rapid reaction, and its half-conversion time is about several seconds or minutes depending on the size of the substituent at the silicon atom and the reaction conditions. The rate of homofunctional condensation (HMFC) of silanols is several orders of magnitude lower. According to our data, trimethylsilanol virtually does not condense at pH 7–14 for a period of several hours, therefore, the data given below characterize a change in the composition of the products caused by homofunctional condensation (3).

Figures 1-3 illustrate the dependences of the relative content (S) of compounds 1a, 2a, and 3a on the amount of acetone in the reaction mixture. The content of hexaorganodisiloxanes is 1 - S. The character of the experimental dependences for the hydrolysis of 1, 2, and 3 is identical.

When the amount of acetone in the reaction mixture is large, at $A > A_{Cli}$ (see Figs. 1, 2), a high content of silanols is observed, and at $A < A_{Cli}$ their content abruptly decreases. These data agree well with the previously obtained results for the hydrolysis of dichlorodiorganosilanes, and are accounted for by the fact that¹ a decrease in A results in a decrease in the water concentration in the organic phase, and at $A < A_{Cli}$ this concentration is not sufficient to hydrolyze chlorosilane completely (see Figs. 1–3). Therefore, the dramatic decrease in the silanol yields is due to the interaction of silanol with the unhydrolyzed starting chlorosilane, which results in the corresponding disiloxane according to reaction (3).

The proposed explanation is correct when the data are obtained in the kinetic field of the reaction.

S(%)



Fig. 1. Dependence of the relative content of Me₃SiOH (S) in the products of hydrolysis of Me₃SiCl on the concentration of Me₂CO (A): $X_1 = 13 \%$ (I), $X_2 = 20 \%$ (2), $X_3 = 30 \%$ (3).



Fig. 2. Dependence of the relative content of Me₂PhSiOH (S) in the products of hydrolysis of Me₂PhSiCl on the concentration of Me₂CO (A): $X_1 = 10 \%$ (I), $X_2 = 30 \%$ (2), $X_3 = 50 \%$ (3), $X_4 = 60 \%$ (4).



Fig. 3. Dependence of the relative content of MePh₂SiOH (S) in the products of hydrolysis of MePh₂SiCl on the concentration of Me₂CO (A): $X_1 = 30 \%$ (1), $X_2 = 50 \%$ (2), $X_3 = 70 \%$ (3).

Determination of the field of hydrolysis of chlorotrimethylsilane

Generally, the limiting stage of a process is determined by a change in the rate constant of the reaction (or conversion),^{3,4,11} but if a plateau is reached, this may rezult both from the «mixer slipping» effect and development of a limiting interphase.³ We proceeded from the fact that in rapid successive-parallel reactions the yield of an intermediate product depends on the uniformity of distribution of the starting components and the reaction products in the reaction mass.¹² In light of this, we selected the relative content S of intermediate product **1a** at the points C_{1j} (see Figs. 1, 4) at X = 27% as the criterion for the boundaries of the limiting stage of the process.

The intensity of mixing of components of a reaction system in an injector is not complicated by the «slipping» effect and depends on the linear rate (V, m s⁻¹) of flow through the nozzle of the injector. The kinetic field of hydrolysis corresponds to S values on the plateau at $V > 1 \text{ m s}^{-1}$ (see Fig. 4). A decrease in the rate of the injective flow results in a loss of kinetic energy and, therefore, in less coverage by the injected flow and a low degree of mixing of the components. The latter, in turn, leads to uneven distribution of the reagents in the bulk of the reaction mass. In the zones with a high content of 1, the compound 1a generated reacts with 1, and the proportion of silanol 1a decreases (see Fig. 4, curves 1, 2). Curve 1 corresponds the direct order of introduction (the injective flow through the nozzle of the injector is a solution of 1 in acetone, the injected flow is aqueous ammonia), and curve 2 corresponds to the reverse order of introduction. In the case of the direct order of introduction, the kinetic condition of hydrolysis is indicated not only by a plateau in curve 1, but also by high values of S.



Fig. 4. Dependence of the relative content of Me₃SiOH (S) in the products of hydrolysis of Me₃SiCl on the rate of reagent flow (V) at X = 27 % obtained under different conditions: *1*, injector, direct introduction; *2*, injector, reverse introduction; *3*, reactor with reflecting partitions; *4*, reactor with a mixer.

The dramatic decrease in the selectivity of hydrolysis with respect to product 1a (see Fig. 4, curve 2) during the reverse order of introduction of the reagents was unexpected. In this case, the over-all consumption of the reagent solutions was the same as for the direct order of introduction, but their bulk ratio (i.e., the injection coefficient) was reversed: $K_1 = 0.45$ and $K_2 = 2.22$. It is to be expected that an increase in the rate of injection should result in an increase in S_{Clii} but in fact this value becomes lower. Apparently, under the experimental conditions, when HMFC of 1a is minimized, a decrease in its yield is caused by the HFPC. It is likely that in the second case, when a continuous phase (aqueous, because X = 27 %) is introduced into the nozzle, the emulsion is characterized by a high hydrodynamic resistance, which results in a perpendicular rate gradient and, therefore, in reverse mixing. The reverse mixing leads to the interaction between the intermediate product 1a and the starting 1 (HFPC) as well as a decrease in S_{CU}

Favorable conditions for the interaction of 1 with 1a should be created when hydrolysis is carried out in an apparatus with a mixer, and the intermediate product is not removed from the reaction zone. Indeed, as in the case of hydrolysis of 1 in the injector, curves 3 and 4show an abrupt increase in the selectivity of hydrolysis as the circular rate of the flow increases, which is followed by a plateau for the kinetic field at the values V = 0.8 to 1.0 m s⁻¹. However, the selectivity remains low (40 %), and, as expected, the selectivity of hydrolysis is higher in the apparatus with reflecting partitions. The low values of S on the plateau are probably caused not only by the «slipping» effect, but also by the procedure employed for the reaction: 1 is constantly introduced into the reactor and inevitably reacts with 1a, which is formed there.

As follows from a comparison of curves 1-4 in Fig. 4, when hydrolysis is carried out in the injector and a dispersion phase is introduced into the nozzle (curve 1), not only do the reagents mix with high intensity, but the products are removed from the reaction zone.

Thus, the data given in Figs. 1-3 correspond to the process of hydrolysis of 1, 2, and 3, which is limited by the rate of the chemical reactions, making it possible to investigate the role of the mass-exchange processes and phase quasiequilibrium.

Determination of the conode regions of phase quasiequilibrium and the reaction zone

To determine the conode regions we used the characteristic points of the S = f(A) plots. In Figs. 1–3 they are the points C_{ji} , which mark the beginning of an abrupt decrease in the proportion of silanols **1a**, **2a**, and **3a** in the products of hydrolysis due to the deficiency of water in the organic phase. In other words, the points C_{ji} for a series of X_i values characterize the same ratio between water and chlorosilane and, therefore, the same organic phase coexisting with the aqueous phase. The experimental data about hydrolysis of dichloromethylphenylsilane¹⁰ give more information and make it possible to plot a considerable number of conodes using the extreme points of formation of oligomers based on the rule of non-equimolarity in heterocopolycondensation processes.

If the inflection points C_{ji} on the S = f(A) dependences are plotted in a Gibbs diagram for each X_i value, their connection will probably give regions of conodes (Fig. 5). The assumption that the lines in the Gibbs diagram are the conode regions is confirmed by the dependences of the yield of silanol S_{Cji} on X (Fig. 6), which indirectly determine the mass ratio between the organic and aqueous phases. Since silanols are mainly formed in the aqueous phase, their yields increase as the aqueous phase volume increases, as is shown in Fig. 6, *i.e.*, the lower the value of X the higher the yield of silanol. The obtained dependence is analogous to the dependence¹⁰ of the product composition in the hydrolysis of dichloromethylphenylsilane on X.

The relative disposition of conodes for 1, 2, and 3 is unexpected and indicates an increase in the mutual solubility of water and chlorosilane as the organic substituent gets larger (see Fig. 5). The same order of disposition of conodes is observed in the dichlorodiorganosilane—water—acetone systems. It was found that the sequence of the disposition of the conodes for 1, 2, and 3 agrees with the tendency for the Hildebrandt parameter, which we have calculated as 14.63, 16.03, and 16.40 J^{1/2} cm^{-3/2}, respectively, to increase. This is apparently associated with the fact that, in the case of the mutual dissolution of the components, the prevailing



Fig. 5. Conode regions of the phase quasiequilibrium for the HPC of R₃SiCl: 1, Me₃SiCl (C_{1i}); 2, Me₂PhSiCl (C_{1i}); 3, MePh₂SiCl (C_{1i}); 4, MePh₂SiCl (C_{2i}); 5, Me₂PhSiCl (C_{2i}).



Fig. 6. Dependence of the relative content of $R_3SiOH(S)$ in the products of hydrolysis of R_3SiCl on the concentration of R_3SiCl in its mixture with water (X): 1, Me_3SiCl (C_{1i}); 2, Me_2PhSiCl (C_{1i}); 3, MePh₂SiCl (C_{1i}); 4, MePh₂SiCl (C_{2i}); 5, Me₂PhSiCl (C_{2i}).

factor is the energy of intermolecular interaction, and not the energy of cavity formation. It is known that the entropy of cavity formation is small for the dissolution of water in organic solvents, which means that the reconstruction of the solvent structure is insignificant.¹³ On the other hand, when organic molecules are dissolved in water, large negative values of the entropy are observed. Therefore, an increase in the bulk of the substituent at the silicon atom would result in a decrease in its solubility in water, while the solubility of water in the organic phase would be determined by intermolecular interactions. This qualitative consideration agrees with the disposition of the conodes for 1 and 2: the replacement of the methyl group in 1 with a phenyl group results in a decrease in the solubility of 2 in the aqueous phase and in an increase in its solubility in the organic phase. Therefore, the conodes for 1 and 2 cross. The analogous feature was also observed for the series of dichlorodiorganosilanes.

The results obtained confirm the heterophasic character of the hydrolysis of mono- and bifunctional chloroorganosilanes, which governs the redistribution of the reagents between the phases. As a result, the formation of oligosiloxanes is either HMFC or HTFC depending on the ratio between water and chlorosilane in the organic phase. The concentrations of the components that are generally used in HPC of chloroorganosilanes enable the formation of oligomers according to the HTFC mechanism.

Thus, the role of the phase state of the reaction system consists of the creation of a field of reagent concentrations according to their activities. Knowledge of the characteristics of the phase quasiequilibrium may allow one to obtain a required component composition in a reaction system and to finely control the composition of the heterophasic reaction products.

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