Concentration oscillations in the condensation of organosilanols

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Auto-oscillations were discovered by TLC in a study of the condensation of $RR'Si(OH)_2$ ($R = R' = Me$, Et, Ph; $R = Me$, $R' = CH_2=CH$, Ph, OH) in aqueous organic solvents in the pH range -1—15 up to large degrees of conversion of the monomer (70—100%). The process is characterized by complicated profiles of the kinetic curves containing sections of acceleration and deceleration of the reaction. The nonequilibrium character of the process was established. It was assumed that the phenomena observed arise as a result of association of the monomer and oligomers during the reaction.

Key words: diorganosilanols, condensation, inhibition, auto-oscillations, association.

Previously,[1] oscillations of concentration have been discovered in the polycondensation of organosilanols:

$$nR_2Si(OH)_2 \rightarrow HO(SiR_2O)_nH + (n - 1)H_2O.$$
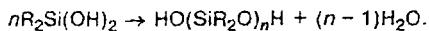
In this communication, we present additional data confirming the occurrence of concentration oscillations (Fig. 1) during the condensation of $RR'Si(OH)$ in aqueous acetone or in aqueous dioxane ($[H_2O]_0 = 16$ mol L^{-1}, $T = 18$—22 °C, aqueous solutions of HCl, KOH, and NH_3 as catalysts).

Experimental

The condensation was carried out in a hermetically sealed microreactor ($V = 5$—10 mL) equipped with a stirrer and maintained at a constant temperature. The variation of the composition of the condensation products was monitored by withdrawing samples and analyzing them by TLC. The TLC analysis was carried out on Silufol UV-254 (30×130 to 200) and RP-18 (50×200 mm, Merck) plates; the samples were applied by Hamilton syringes with siliconized needles. The following eluents were used: dioxane—toluene (7 : 1) to separate difunctional silanols and toluene—acetonitrile—diglyme (2.75 : 1 : 1) to separate products of condensation of $PhSi(OH)_3$. When RP-18 plates were used, elution was carried out by acetonitrile or its mixture with water (4 : 1). Visualization of the spots of substances and their quantitative processing were carried out by two procedures. 1. The spots of $HO[SiPhRO]_nH$ (L_n) were scanned using a Shimadzu CS-9000 double-beam densitometer ($\lambda = 254$ nm); the composition was determined by normalization with correction factors ($f_n = P_nS_1/P_1S_n$, where P is the weight of the sample in g, S is the reading of the dinsitometer) for each compound. The relative error in the average proportion of L_n was 0.5—7.0% (found for check solutions).
2. To determine the composition of the products $HO—[SiRR'O]_n—H$ containing no chromophore groups, the

calibration dependences $\sqrt{F_n} = a_n + b_n(\lg P_n + 5)$ were used; F_n and P_n are the area of the spot (mm^2) and the weight of the component ($5 \cdot 10^{-6}$—$1 \cdot 10^{-4}$ g), respectively; a and b are regression coefficients. Regression equations were obtained using 545 reference points. For example, the coefficients for methylphenylsiloxanediols $HO[SiPhMeO]_nH$ are: $a_1 = 2.7\pm0.4$, $b_1 = 3.6\pm0.1$; $a_2 = 2.6\pm0.6$, $b_2 = 4.3\pm0.1$; $a_{3,4} = 3.1\pm0.7$, $b_{3,4} = 4.8\pm1.3$. The correlation coefficients (R) of the regression equations are 0.91 ($n = 1$), 0.85 ($n = 2$), and 0.84 ($n = 3$ and 4); standard deviation 15—30%.

An increase in the accuracy of the analysis was achieved by determining the relative molar composition of the condensation products. Analysis of test mixtures of known compositions showed that the error of determination was 1—7% (relative) and did not depend on the ratio of the components or the weight of the sample applied on the plate within the limits mentioned above. It was also found that during the period of the analysis of a sample (10—15 min), no noticeable condensation of diols on the plates occurs. At high concentrations of catalysts, no chemical transformations of acetone or dioxane were observed over the period required for complete conversion of $R_2Si(OH)_2$ (1—10 min).

The current concentrations of the condensation products (C_n/mol L^{-1}) needed to construct kinetic curves $C_n = f(t)$ were calculated from the initial concentration of the monomer C_0, the material balance relationships, and normalization conditions:

$$C_0 - C_1 = 2C_2 + 3C_3 + \ldots + nC_n; \quad \Sigma(C_n/\Sigma C_n) = 1.$$

The solution of this set of equations for each C_n is an awkward algebraic expression; therefore, we do not present it here. Organosilanols and organosiloxanols $HO[SiPhRO]_nH$ (L_n) were synthesized by the hydrolysis of the corresponding diorganodichlorosilanes and diorganodichlorosiloxanes according to published procedures[2] and by an original procedure involving hydrolysis by a twofold amount of water in diisopropyl ether or in ethyl acetate in the presence of alkene oxides as acceptors of HCl. Organosiloxanols $HO[SiRR'O]_nH$ with $n = 3$—4 were isolated in a pure state by preparative liquid chro-
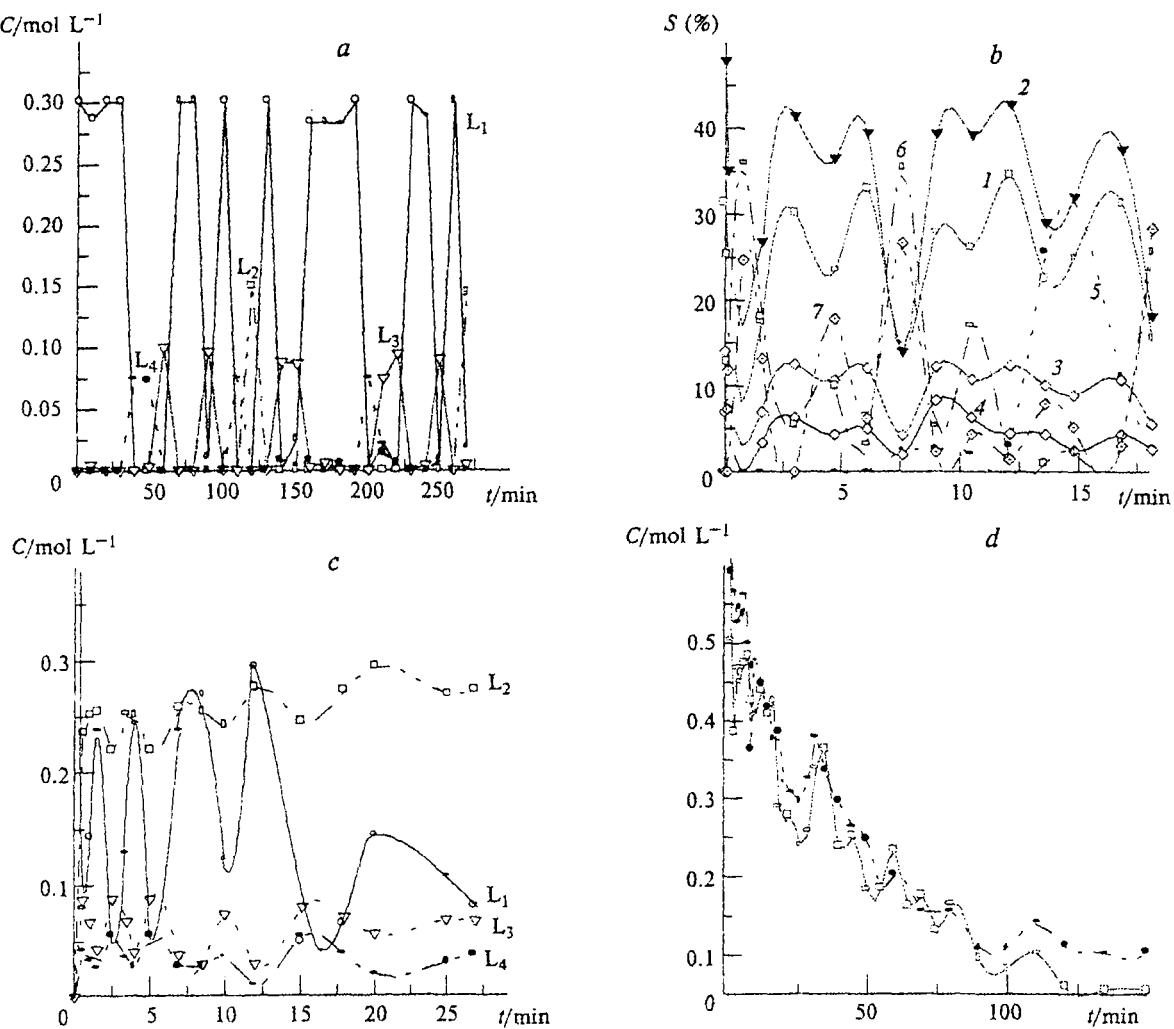
Fig. 1. Oscillational kinetic curves: *a*, $PhSi(OH)_3$ in dioxane, $C_0 = 0.3$ mol L^{-1}, $[H_2O]_0 = 10^{-2}$ mol L^{-1}, without a catalyst; *b*, $(PhSi(OH)O)_4$ in acetone, $C_0 = 0.3$ mol L^{-1}, $[H_2O]_0 = 10^{-2}$ mol L^{-1}, $[HCl] = 10^{-2}$ mol L^{-1}, *cis*-isomer $(PhSi(OH)O)_4$ (*1*), *trans*-isomers $(PhSi(OH)O)_4$ (*2—4*), unidentified compounds (*5—7*); *c*, $MePhSi(OH)_2$ in acetone, $C_0 = 0.98$ mol L^{-1}, $[H_2O]_0 = 16$ mol L^{-1}, pH = 0.7; *d*, two examples of reproducibility of experimental results in the case of $Et_2Si(OH)_2$ in acetone, $C_0 = 0.7$ mol L^{-1}, $[H_2O]_0 = 16$ mol L^{-1}, pH = 0.9. *S* is the proportion, % (w/w). L_n — $HO[SiRR'O]_nH$.

matography. The purity of the products was estimated by TLC, HPLC, ^{29}Si NMR, and by measuring their melting points.

Results and Discussion

The concentration oscillations shown in Fig. 1 were detected occasionally by analyzing solutions of $R_2Si(OH)_2$ both with and without a catalyst from time to time. Attempts to reproduce the auto-oscillations of the concentrations of the monomer and condensation products were seldom successful and resulted in a change in the composition of the condensation products and in the period and amplitude of oscillations. The good reproducibility of the complicated profile of the curve for the consumption of $Et_2Si(OH)_2$ (see Fig. 1, *d*) is the only exception. However, the large amplitude of variation of

the concentrations of the monomers and the substantial difference between the R_f values of compounds (Fig. 2) rule out the alternative assumption that the observed concentration oscillations are due to experimental errors. Even a visual analysis of chromatographic plates
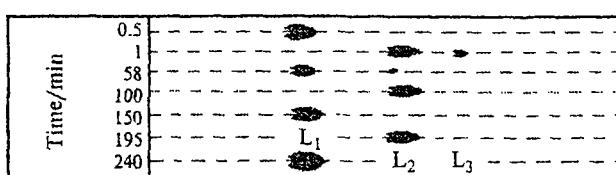

Fig. 2. Chromatograms (TLC) for the time variation of the composition of the products of condensation of $PhSi(OH)_3$ in aqueous acetone without a catalyst; $C_0 = 0.09$ mol L^{-1}, $[H_2O]_0 = 10^{-2}$ mol L^{-1}. L_n — $HO[SiPh(OH)O]_nH$.
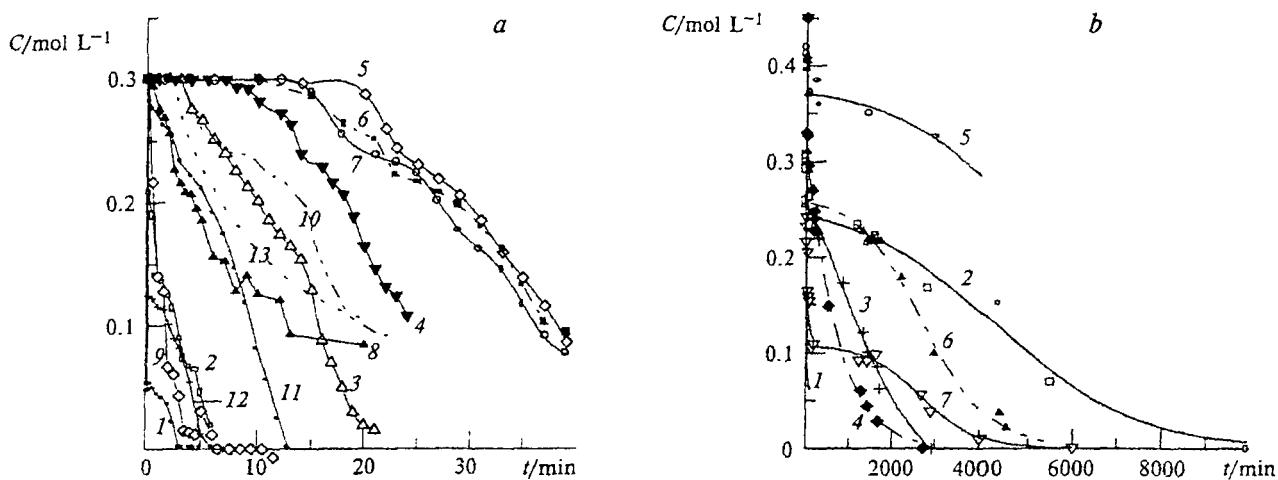
Fig. 3. Kinetic curves for the condensation: *a*, PhSi(OH)₃, C_0 = 0.3 mol L⁻¹, dioxane—water, $[H_2O]_0$ = 16 mol L⁻¹, pH = 1.1 (*1*), 1.4 (*2*), 2.0 (*3*), 2.5 (*4*), 4.0 (*5*), 5.0 (*6*), 6.0 (*7*), 7.0 (*8*), 9.0 (*9*); $[H_2O]_0$ = 8.75 mol L⁻¹, pH = 7.0 (*10*); acetone—water, pH = 2.0 (*11*); DMF—water, pH = 2.0 (*12*); without a catalyst, in anhydrous acetone (*13*); *b*, Me₂Si(OH)₂, C_0 = 0.9 mol L⁻¹, acetone—water, $[H_2O]_0$ = 16 mol L⁻¹, pH = 1.6 (*1*), 2.6 (*2*), 3.2 (*3*), 4.8 (*4*), 7.4 (*5*), 13.0 (*6*), 14.3 (*7*). L_n — HO[SiRR'O]ₙH.

(see Fig. 2) unambiguously indicates that PhSi(OH)₃ periodically disappears and appears again in the reaction mixture, and this is accompanied by the appearance and disappearance of the condensation products, oligosiloxanes L_n, respectively (see Fig. 1, *a—c*).

Concentration oscillations of PhSi(OH)₃ and tetrahydroxytetraphenylcyclotetrasiloxane with large amplitudes (see Fig. 1, *a*, *b*) were detected in our experiments for low concentrations of an acid catalyst and water. In the case of MePhSi(OH)₂ (see Fig. 1, *c*) and Et₂Si(OH)₂ (see Fig. 1, *d*), an auto-oscillation regime of the condensation of RR'Si(OH)₂ was also observed at high concentrations of an acid catalyst and water. In the presence of an alkaline catalyst, concentration oscillations have not yet been observed.

Thus, the phenomenon of concentration oscillations in chemical reactions[3] has also been found in polycondensation. Although the currently available experimental data are still inadequate to provide an explanation for this phenomenon, some prerequisites necessary for the auto-oscillations to occur can be listed. First, the system should involve protonated intermediates and associated forms of the reactants with various acid-base properties; this can make this system unstable owing to the competition of the starting compounds for the interaction with intermediates.[4] Second, the obtained kinetic curves should be characterized by an induction period and by sections of acceleration and deceleration of the reaction (Fig. 3, *a*). It was found that at the beginning of the acid-catalyzed condensation of R₂Si(OH)₂, the pH of the medium sharply decreases (by ~0.3—0.5 pH units), which implies that the catalyst forms an inactive complex with the monomer or with the reaction product. The periods of acceleration and deceleration of the reaction can also result in the occurrence of oscillations of the concentrations of reactants and reaction products.

We assume that the complicated profiles of the kinetic curves are due to the participation of associated forms of the monomer and oligomers in the process. According to the concept of the role of molecular organization of the reactants in liquid-phase reactions,[5] we assume that the reaction system contains associates, whose structure is close to that of prereactive complexes and which are located on the reaction pathway (exit channels). The prereactive complexes can be formed by hydrogen or donor-acceptor bonds. Within the framework of this concept, existence of nonreactive com-
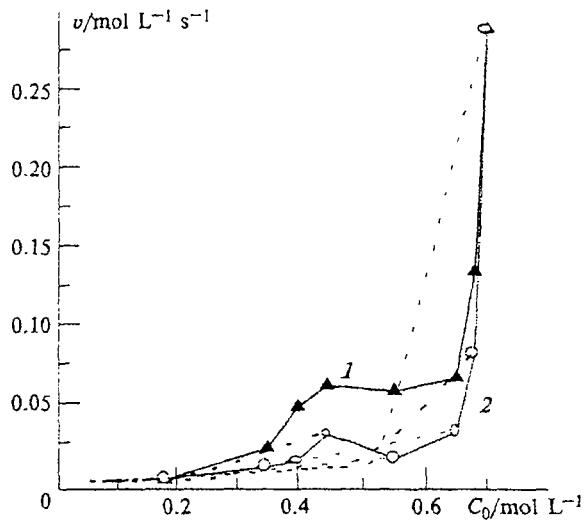

Fig. 4. Dependences of the initial (solid line) and current (dashed line) rates of condensation of Et₂Si(OH)₂ on its initial and current concentrations, respectively, obtained by differentiation of experimental (*1*) and averaged (*2*) kinetic curves by the function $C = C_\infty + \sum_i C_i e^{-k_i t}$ (n = 2); pH = 0.9.

plexes (accumulation channels) is also considered. The ratio of these types of complexes depends on the concentrations of the reactants in the solution.

In conformity with the above-described concept of the molecular organization of reactants, the routes of condensation of $R_2Si(OH)_2$ and, possibly, its self-acceleration are exit channels. The routes of retardation of the reaction observed in our experiments are accumulation channels. This assumption is confirmed by the complex dependence of the rate of condensation of $Et_2Si(OH)_2$ on its concentration (Fig. 4). It can be seen from Fig. 4 that the dependences of the initial and current reaction rates on the concentrations of $Et_2Si(OH)_2$ are different. This means that intermediate species have an effect on the rate of the process. The complex shape of the $v = f(C)$ dependence and the sharp increase in the rate of condensation of $Et_2Si(OH)_2$ following an increase in the monomer concentration may be due to the association of the monomer and oligomers resulting in the change in their acid-base properties and their reactivity.

It should also be noted that when the degree of conversion of the monomer is larger than 70%, the reaction mixture separates into layers. In addition, the concentrations of oligomers formed in the homogeneous solution are markedly higher than their solubility in the

system. Thus, the condensation of $RR'Si(OH)_2$ occurs in a solution existing in a metastable state, which could also be the reason for the observed concentration oscillations.

Thus, the complicated profiles of the kinetic curves and the complex dependence of the reaction rate on the monomer concentration point to a complex molecular organization of the reactants during the condensation of $RR'Si(OH)_2$ both in aqueous and in nonaqueous media. However, the experimental data obtained by now do not make it possible to draw full and unambiguous conclusions about the mechanism of the process as a whole.

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