CONVERSION OF POLYORGANOSILOXANES IN AGGRESSIVE MEDIA

COMMUNICATION 2. KINETICS OF THE HYDROLYSIS OF OCTAMETHYLCYCLOTETRASILOXANE IN AQUEOUS DIOXANE SOLUTIONS OF SULFURIC ACID

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In the hydrolysis of octamethylcyclotetrasiloxane $[(CH_3)_2SiO]_4$ (I) in aqueous solutions of weak acids under heterogeneous conditions, a water molecule participates in the limiting step of the acid-catalyzed cleavage of the siloxane bond by an S_N2 mechanism [1].

We were interested in determining the principles of the acid-catalyzed hydrolysis of (I) under homogeneous conditions. The present work is devoted to a study of the kinetics of the hydrolysis of (I) in aqueous dioxane solutions with various contents of water and sulfuric acid.

EXPERIMENTAL

We used (I) (bp 176°), $[(CH_3)_2SiO]_5$ (II) (bp 101°, 20 torr), and $[(CH_3)_2SiO]_6$ (III) (bp 128°, 20 torr). To prepare the solutions we used grade very pure H_2SO_4 and scintillation grade dioxane.

The kinetics of the hydrolysis of (I) was studied in aqueous dioxane solutions at 29-80° in the interval of H_2SO_4 concentrations 10^{-4}-10^{-1} M. The decrease in (I) in the reaction mixture was determined by the method of gas—liquid chromatography according to the height of the peak, as an average of 3-4 measurements (LKhM-7A, detector katharometer, column with brand INZ-600 carrier, treated with PMS-100 polysiloxane liquid, carrier gas He, 40-60 ml/min, 120°). The experiments were conducted in thermostatically controlled cells. The temperature of the solution was maintained with an accuracy of ±0.1°. The samples were cooled to ~20° and analyzed. Cooling to a constant temperature in the analysis of the samples is necessary since dioxane has a large coefficient of expansion. The electric conductivity of an aqueous dioxane solution (10 M H_2O) of sulfuric acid was determined on a Radelkis-OH 102/1 conductometer.

DISCUSSION OF RESULTS

In the acid-catalyzed hydrolysis of (I), an assortment of linear and cyclic oligomers of polydimethylsiloxane can be formed. It is of interest to determine, on the one hand, the composition of the reaction

TABLE 1. Equilibrium Composition* of the Reaction Products of the Hydrolysis of (I) in Aqueous Dioxane Solutions of H_2SO_4 as a Function of the Water Content

Water content, M	(I), %	(II), %	Water content, M	(I), %	(II), %
2,54	69	27	7,48	60	36
4,93	65	31	10,0	56	40

*Average error ± 2%.

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TABLE 2. Kinetic Parameters of the Hydrolysis of Cyclic Organosiloxanes in Media of Various Compositions

Oligomer	$c_{H_2SO_4}\cdot 10^2$, M	c_{H_2O}, M	$k^{25°}_{eff_1}\cdot 10^4$, min^{-1}	E, kcal /mole	Oligomer	$c_{H_2SO_4}\cdot 10^2$, M	c_{H_2O}, M	$k^{25°}_{eff_1}\cdot 10^4$, min^{-1}	E, kcal /mole
(I)	22	10	40	9,3	(I)	9,9	4,93	14	8,0
	11	10	34			4,8	4,93	12	
	4,8	10	18			2,4	4,93	8,4	
	2,61	10	14			1,0	4,93	5,2	
	1,2	10	11			0,6	4,93	3,5	
	0,48	10	4,6			8,9	2,54	5,3	10,7
	0,24	10	2,0			5,2	2,54	5,3	
	0,12	10	0,97			0,82	2,54	2,1	
	0,038	10	0,41		(II)	5,72	2,54	15	10
	4,8	7,48	15,0	9,0	(III)	5,72	2,54	8,7	11

products, and on the other to determine the influence of components of the solution and temperature on the direction of the reaction. Gas—liquid chromatographic analysis showed that the equilibrium composition of the reaction products is practically independent of the H_2SO_4 concentration and the temperature but varies somewhat with the water – dioxane ratio. The degree of conversion of (I) increases with increasing water content in solution (Table 1). The basic reaction product is the cyclic oligomer (II); the content of the remaining cyclic and linear oligomers does not exceed 4%. In special experiments on the investigation of the kinetics of the conversion of the cyclic oligomers (II) and (III) in aqueous dioxane solutions of H_2SO_4 of analogous composition, the same equilibrium composition of the reaction products was obtained as in the hydrolysis of (I).

In the acid-catalyzed hydrolysis of (I) the main product formed is (II); the process of conversion of (I) can be represented in a first approximation as a reversible first-order reaction. For a calculation of the effective summary constant (k_{eff}) we used two methods. If the reaction reached equilibrium, k_{eff} was calculated according to the equation for a reversible first-order reaction; if the reaction proceeded slowly, then the Guggenheim method [2] was used for the calculation of k_{eff}. The effective rate constant k_{eff} of the forward reaction was calculated either according to the initial portion of the kinetic curve or using the equilibrium constant. The agreement between k_{eff_1}, obtained by various methods, is satisfactory. The activation energies (Table 2) were calculated according to the Arrhenius equation. For a calculation of the rate constant, which does not depend on the acid concentration, it is necessary to have information on the H^+ ion concentration. It is known that hydrochloric and nitric acids [3, 4] are not entirely dissociated in media with a low dielectric constant. Therefore, we were interested in measuring the dissociation constant of H_2SO_4.

Determination of the Dissociation Constants of H_2SO_4 in Aqueous Dioxane Solutions. In solutions with a low dielectric constant, strong electrolytes are associated at such concentrations of ions as 10^{-4} N; therefore, the limiting Ostwald dilution law is not accurate, and to calculate the dissociation constant of H_2SO_4 from data on the electric conductivity we used the method of [3, 5]

$$\frac{F(z)}{\lambda} = \frac{1}{\lambda_0} + \frac{C\lambda Y_{\pm}^2/F(z)}{K_a(\lambda_0)^2} \qquad (1)$$

$$\lg Y_{\pm} = -\delta(f)\sqrt{\alpha C} \qquad (2)$$

$$\alpha = \frac{\lambda}{\lambda_0 F(z)} \qquad (3)$$

$$z = \delta(\Lambda)\sqrt{C\lambda}/\lambda_0^{3/2};\ F(z) = {}^4/_3 \cos^2 {}^1/_3 \arccos\left(-\frac{3\sqrt{3}}{2}z\right).$$

TABLE 3. Dependence of the Equivalent Electric Conductivity, Activity Coefficients, and Concentration Dissociation Constant on the H_2SO_4 Concentration in Aqueous Dioxane Solution (10 M H_2O)

$c_{H_2SO_4}\cdot 10^4$, M	λ, $cm^2/\Omega\cdot mole$	$Y_{\pm}^2$	$K_C\cdot 10^4$ M	$c_{H_2SO_4}\cdot 10^4$, M	λ, $cm^2/\Omega\cdot mole$	$Y_{\pm}^2$	$K_C\cdot 10^4$ M
1,47	33,5	0,558	3,8	246	12,6	—	—
4,39	27,0	0,395	5,3	364	12,4	—	—
10,4	22,2	0,262	8,0	729	12,2	—	—
24,3	18,8	0,136	15,0	731	12,2	—	—
76,0	14,6	—	—	$3,77\cdot 10^3$	9,29	—	—

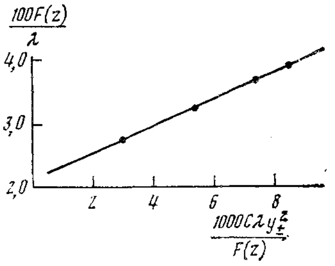

Fig. 1

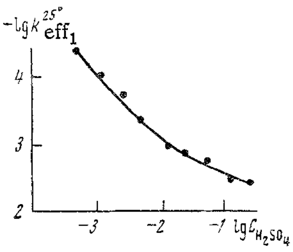

Fig. 2

Fig. 1. Graphical determination of the thermodynamic dissociation constant and equivalent electric conductivity at infinite dilution for aqueous dioxane solutions of H_2SO_4 (10 M H_2O).

Fig. 2. Dependence of the effective rate constant of the forward reaction on the acid concentration at 25° in logarithmic coordinates.

where λ is the equivalent electric conductivity, $cm^2/\Omega \cdot mole$, λ_0 is the limiting equivalent electric conductivity at infinite dilution, $cm^2/\Omega \cdot mole$; C is the acid concentration, g-eq/liter; K_a is the thermodynamic dissociation constant; $Y_{\pm}$ is the average molar activity coefficient of the electrolyte; $\delta(\Lambda)$ is the Onsager coefficient; α is the degree of dissociation of the acid; and $\delta(f)$ is the coefficient in the limiting Debye – Hückel law.

The upper limit of the applicability of Eq. (1) is considered to be $C = 1.2 \cdot 10^{-14} (\varepsilon T)^3$ g-eq/liter [3], where ε is the dielectric permeability of the medium. In view of this, it did not seem possible to measure the thermodynamic constants of H_2SO_4 in all the solutions studied. K_a was measured only for an aqueous dioxane solution containing 10 M H_2O.

The value of λ_0 was found by successive approximations; the value obtained by approximate extrapolation of the data on electric conductivity (Table 3) was taken as the initial value. In the calculation it was assumed that H_2SO_4 is dissociated primarily according to the first step. The data obtained fit well into the coordinates of Eq. (1) (Fig. 1), which supports this hypothesis. The experimental data are described by a straight line intercepting a segment $1/\lambda_0 = 2.1 \cdot 10^{-2}$ $\Omega \cdot mole/cm^2$ on the Y-axis and possessing a slope equal to $1/K_a \cdot (\lambda_0)^2 = 2.16$. These values correspond to $\lambda_0 = 47.5$ $cm^2/\Omega \cdot mole$ and $K_a = 2.1 \cdot 10^{-4}$ M. If aqueous solutions of acids are considered close to ideal up to a concentration of $1 \cdot 10^{-2}$–$1 \cdot 10^{-1}$ N, and in them $a_{H^+} = C_{H^+}$, then in nonaqueous media, especially with low dielectric constants, these values may differ appreciably. Then $K_a = a_{H^+} a_{A^-}/a_{HA}$ will differ from the concentration dissociation constant $K_C = K_a \cdot (Y_{\pm}^2/Y_{HA})$. Moreover, if K_a is constant, then the value of K_C varies within the entire concentration interval, while $\lim_{C \to 0} K_C \to K_a$. From the data of the electric conductivity, using Eq. (2), we calculated $Y_{\pm}^2 (Y_{HA} = 1)$ and K_C (see Table 3).

From Fig. 2 it is evident that the dependence of $k_{eff_1}^{25°}$ on the acid concentration is nonlinear. Such a variation of $K_{eff_1}^{25°}$ with C_{HA} may be due, in particular, to the appreciable protonation of the Si—O—Si bond. However, in aqueous solutions at a H_2SO_4 concentration of 55%, no protonated form was detected [1]. It would be difficult to expect that in aqueous dioxane solutions, containing up to $2.2 \cdot 10^{-1}$ M H_2SO_4, protonation would be observed. To confirm this, aqueous dioxane solutions of (I) in the presence of H_2SO_4 were studied by the PMR method. The absence of a change in the chemical shift of (I) in the case of measurement in the initial time segment is evidence in support of this hypothesis. Another explanation of the nonlinear relationship of $k_{eff_1}^{25°}$ to the acid concentration is reduced to the fact that in aqueous dioxane solutions the acid is not entirely dissociated. Then the nonlinear nature of the dependence of $k_{eff_1}^{25°}$ on the H_2SO_4 concentration is associated with a change in its degree of dissociation.

It is known that the reaction proceeds according to a bimolecular mechanism [1]

$$k_{eff_1} = \frac{k_{true}}{K_B} a_{H_2O} h_0 \frac{f_{BH^+}}{f^{\neq}} \tag{4}$$

For acid-catalyzed reactions, it is frequently assumed that $f_{BH^+}/f^{\neq} = \text{const}$. If we assume that in the solutions studied $h_0 = C_{H^+}$, while $a_{H_2O} = C_{H_2O}$, then Eq. (4) takes the following form

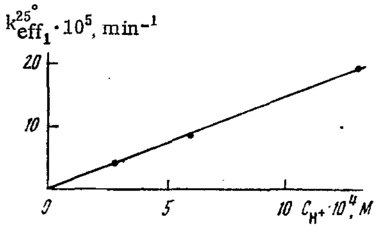

Fig. 3

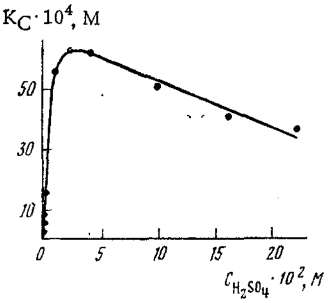

Fig. 4

Fig. 3. Dependence of the effective rate constant of the forward reaction on the H$^+$ concentration (for known concentrations).

Fig. 4. Dependence of the concentration dissociation constant on the acid concentration.

$$k_{eff_1} = \frac{k_{true}}{K_B} C_{H_2O} C_{H^+} \frac{f_{BH^+}}{f^{\neq}} \tag{5}$$

where k_{true} is the rate constant, which does not depend on the acid concentration; K_B is the basicity constant of the reagent; f_{BH^+} and $f^{\neq}$ are the activity coefficients of the protonated form and activated complex, respectively. In this region of C_{HA}, where K_C is known to us, we determined the H$^+$ concentration:

$$C_{H^+} = \frac{-K_C \pm \sqrt{K_C{}^2 + 4K_C C_{HA}}}{2} \tag{6}$$

As can be seen from Fig. 3, $k^{25°}_{eff_1}$ is directly proportional to C_{H^+}, and k_{true}/K_B can be determined from the slope. This in turn permits a determination of K_C, α, and $Y_\pm$ in the region of more concentrated solutions. The dependence of K_C on C (Fig. 4) is characterized by the presence of a maximum, showing that the summary effect of weakening of coulombic forces is extremely substantial. This effect is associated with a change in the dimensions of the ions and an increase in the concentration of the solution, causing an increase in the activity of the acid. Although K_C and $Y_\pm$ change rather substantially in the concentration region from $3.8 \cdot 10^{-4}$ to $5 \cdot 10^{-3}$ M, α remains practically unchanged; therefore, the slope (see Fig. 2) in this concentration region is close to one. At a higher acid concentration, beginning with $2.1 \cdot 10^{-2}$ M it becomes ~0.5. This is due to the fact that Eq. (6) is simplified to $C_{H^+} = \sqrt{K_C C_{H_2SO_4}}$.

It is interesting to note that in solutions with a lower water content the slopes are close to 0.5. Unfortunately it is difficult to compare the data obtained in different media on account of the impossibility of determining K_C in aqueous dioxane solutions with water contents of 2.54, 4.93, and 7.48 M.

The reaction probably proceeds according to the following scheme:

$$n\,[(CH_3)_2SiO]_4 \rightleftarrows n HO[(CH_3)_2SiO]_4H \rightleftarrows HO\,[(CH_3)_2SiO]_{4n}H \rightleftarrows \frac{4}{5} n[(CH_3)_2SiO]_5$$

but since the intermediate steps are rapid, only the final result of the formation of two rings is visible.

CONCLUSIONS

1. The kinetics of the hydrolysis of octamethylcyclotetrasiloxane in aqueous dioxane solutions was studied.

2. In the course of the hydrolysis of octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane is formed, and with increasing water concentration the equilibrium is shifted toward the formation of decamethylcyclopentasiloxane.

3. The rate constants of the forward and reverse reactions and the activation energies of the processes were determined.

4. The dissociation constants of sulfuric acid according to the first step were measured in an aqueous dioxane solution containing 10 M water.

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