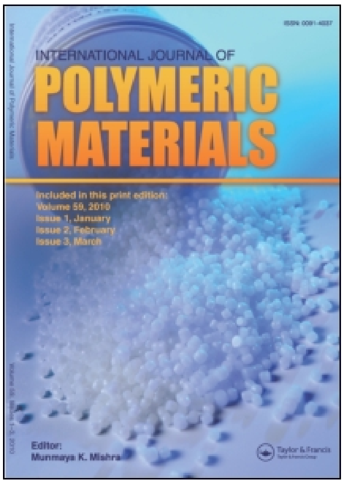

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Investigation of Organosiloxane Equilibrium Reactions

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A systematic study of the regularities of the equilibrium rearrangement reaction of monomeric and oligomeric organosilicon compounds was carried out. The reactions were carried out in the presence of nucleophilic and electrophilic catalysts. An overview of the experimental data is used to determine the features common to all reactions under consideration.

Keywords: Organosiloxanes; equilibrium rearrangements; catalysts; nucleophilic and electrophilic; reaction centers

1. INTRODUCTION

We extensively studied the regularities of the equilibrium rearrangement reactions of monomeric and oligomeric organosilicon compounds with $\equiv$Si—O—Si$\equiv$, $\equiv$Si—Cl, $\equiv$Si—O bonds participation. The reactions were carried out in the presence of nucleophilic and electrophilic catalysts. The results of these studies are presented in publications [1-10].

These reactions are widely used in laboratory and industrial practices for directed synthesis of a variety of organosilicon compounds. However, in spite of the widespread use of these reactions their regularities at quantitative levels have not been adequately investigated. There are no articles where a correlation between the regularities of equilibrium rearrangement reactions and participation of the most broadly used reactive bonds at silicon $\equiv$Si—O—Si$\equiv$, $\equiv$Si—Cl, $\equiv$Si—O— is carried out. In the present article we analyse the principal results of our published and unpublished investigations. This data allows us to determine the features common to all reactions under consideration.

2. FUNDAMENTALS

2.1. Investigations on Equilibrium Reactions at Catalytic Rearrangements of Organodisiloxanes

Asymmetrical organodisiloxanes are obtained by the cohydrolysis [11], cocondensation [12] and catalytic redistribution reactions in the presence of nucleophilic or electrophilic catalysts [13]. The last reaction allows one to obtain these compounds quantitatively due to the reuse of unreacted reagents.

The effect of substituent nature on the process of asymmetrical organodisiloxanes formation through reaction of symmetrical organodisiloxane, catalyzed by heterogenous electrophilic catalysts – sulphocationite "KU-23" (sulphonated copolymer of styrene with divinylbenzene with sulphogroup containing 3.8 mg-eq/l and 7wt.% water) has been studied. The reactions of pentamethyldisiloxane (I) formation through 1, 1, 3, 3-tetramethyldisiloxane interaction with hexamethyldisiloxane (system A); 1-chloromethyl-1, 1, 3, 3-tetramethyldisiloxane (II) at 1, 1, 3, 3-tetramethyldisiloxane interaction with 1, 3-bis-(chloromethyl) tetramethyldisiloxane (system B); pentamethyl (chloromethyl)-disiloxane (III) at hexamethyldisiloxane interaction with 1, 3-bis(chloromethyl)-tetramethyldisiloxane (system C) and pentamethyl (chloroformiatomethyl)disiloxane (IV) at hexamethyldisiloxane interaction with 1, 3-bis (chloroformiatomethyl)tetramethyldisiloxane (system D) have also been studied. The reaction may be shown as follows:

$$\underset{\text{M}}{\text{X SiMe}_2\text{OSiMe}_2\text{X}} + \underset{\text{L}}{\text{Y SiMe}_2\text{OSiMe}_2\text{Y}} \overset{\text{Cat}}{\Leftarrow = = \Rightarrow} \underset{\text{Q}}{2\text{X SiMe}_2\text{OSiMe}_2\text{Y}} \quad (1.1)$$

The reaction is conducted without solvent at temperatures over 10–40 °C in the presence of 5 mass % of "KU-23" sulphocationite. The reaction proceeding is controlled by GLC method against the changes in the contents of initial symmetrical and formed asymmetrical organodisiloxanes. Time of reaction systems arriving to the equilibrium is diminished in a series.

$$\underset{\text{“A”}}{(Me_3Si)_2O + (HMe_2Si)_2O} > \underset{\text{“C”}}{(HMe_2Si)_2O + (ClCH_2SiMe_2)_2O}$$

$$> \underset{\text{“B”}}{(Me_3Si)_2O + [ClC(O)OCH_2SiMe_2]_2O} > \underset{\text{“D”}}{(Me_3Si)_2O + (ClCH_2SiMe_2)_2O}$$

Due to electrophilic nature of the catalysts reactivity for the organodisiloxane pair under consideration should be diminished with diminishing of electronodonor properties of oxygen atom in siloxanes and should be the lowest for the system $(HMe_2Si)_2O$—$(ClCH_2SiMe_2)_2O$ (B), since the intial siloxanes have more electronoacceptor substituents X and Y (H and $ClCH_2$, respectively) at silicon. Characteristically, however, high reactivity is observed for this pair. The lowest reactivity is observed for pair $(Me_3Si)_2O$—$(ClCH_2SiMe_2)_2O$. Observed order of the change in reactivity allows us to suggest that the reaction rate is considerably determined by substituent sizes (X and Y) at silicon. Equilibrium content of compound (II) for B system is near to the calculated for the statistical composition. Value of the equilibrium constant is equal to 4.7 ± 0.7 and is near to the constant value at statistical composition (4.0). For A, C and D systems equilibrium content of asymmetrical organodisiloxanes is higher than calculated one. Values of the constants are higher than at the statistical composition and amounted to 5.4 ± 1.0; 6.5 ± 1.0 and 5.5 ± 1.0 respectively. The kinetic parameters of this reaction have been investigated. According to the scheme (1.1) the process under consideration is a reversible reaction of the second order and is described in [14] by equation (1.2)

$$\frac{dx}{dt} = k(M_0 - x)(L_0 - x) - k'x^2 \qquad (1.2)$$

Integral form of equation (1.2) has the following form:

$$\mathrm{In}\left(\frac{|\bar{x}|}{|\bar{x}'|}\frac{|\bar{x}' - x|}{|\bar{x} - x|}\right)\cdot\left(\frac{1}{\bar{x}' - \bar{x}}\right) = a \cdot t \quad \text{or} \quad F(x) = a \cdot t \qquad (1.3)$$

where

$$x = M_0 - M = L_0 - L = 0,5Q \tag{1.4}$$

$$\bar{x} = M_0 - M_p = L_0 - Lp = 0,5Q_p \tag{1.5}$$

$$\bar{x}' = \frac{4K(M_0 + L_0)}{K - 4} - \bar{x} \tag{1.6}$$

$$K = k/k' = Q_p^2/(M_p \,.\, L_p) \tag{1.7}$$

$$a = k - 4k', \quad k' = a/(K - 4), \quad k = a - 4k' \tag{1.8}$$

M_0, L_0 – initial; M, L, Q – running; M_e, L_e, Q_e – equilibrium concentrations of organodisiloxanes in reaction mixture (equation (1.1); k, k′ – rate constants of direct and reverse reaction; K – equilibrium constant; t – time.

Experimental data show that in accordance with reaction scheme the process with high correlation coefficient (r) is described by the equation (1.3). Values of rate constants of direct and reverse reaction esfimated by equation (1.4–1.8) are presented in Table 1.1. From Table 1.1 it follows that the obtained rate constants of reactions depend on initial ratios of starting reagents.

Correlation of rate constants of reverse reactions (on equation (1.1) showed that the reactivity change of asymmetrical organodisiloxanes is as follows:

$$(I) > (II) > (IV) > (III)$$

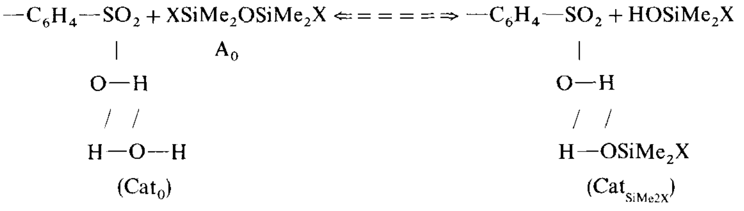
Study of the B system at different temperatures showed that equilibrium constant values are essentially unaffected by temperature. Thus, a conclusion is made that the process is determined by entropy factor since reaction enthalpy is near the zero. The same values of activation energy of direct (ΔE) and reverse ($\Delta E'$) reactions (44.8 kJ/mol) point out to the zero value of the reaction enthalpy. Observed dependence of reaction

TABLE 1.1 Rate constants of direct (k) and reverse (k′) reations and equilibrium (K) of reactions of redistribution of symmetrical organodisiloxanes

Initial concentration of organodisiloxanes l/mol. sec		*t, °C*	*r*	*k* *l/mol. sec.*	*k′* *l/mol. sec.*	*K*
M_0, mol/l	*L_0, mol/l*					
System A: $HMe_2SiOSiMe_2H + Me_3SiOSiMe_3$						
4.39	0.99	12	0.999	$14.3 \cdot 10^{-4}$	$2.6 \cdot 10^{-4}$	$5.4 \pm 1,0$
2.91	2.12	12	0.979	$12.7 \cdot 10^{-4}$	$2.4 \cdot 10^{-4}$	
1.01	3.81	12	0.984	$9.5 \cdot 10^{-4}$	$1.8 \cdot 10^{-4}$	
System B: $HMe_2SiOSiMe_2H + ClCH_2Me_2SiOSiMe_2CH_2Cl$						
4.39	1.02	22	0.999	$14.0 \cdot 10^{-5}$	$3.0 \cdot 10^{-5}$	4.7 ± 0.7
3.86	1.75	22	0.993	$16.0 \cdot 10^{-5}$	$3.4 \cdot 10^{-5}$	
2.42	2.50	22	0.999	$25.0 \cdot 10^{-5}$	$5.3 \cdot 10^{-5}$	
1.67	3.17	22	0.982	$34.5 \cdot 10^{-5}$	$7.3 \cdot 10^{-5}$	
0.99	3.68	22	0.996	$67.0 \cdot 10^{-5}$	$14.2 \cdot 10^{-5}$	
2.63	2.46	33	0.997	$52.8 \cdot 10^{-5}$	$11.2 \cdot 10^{-5}$	4.4
2.68	2.42	39	0.998	$81.7 \cdot 10^{-5}$	$17.4 \cdot 10^{-5}$	4.4
System C: $Me_3SiOSiMe_3 + ClCH_2Me_2SiOSiMe_2CH_2Cl$						
3.80	0.95	22	0.999	$5.0 \cdot 10^{-7}$	$7.7 \cdot 10^{-8}$	6.5 ± 1.0
3.01	1.69	22	0.992	$6.2 \cdot 10^{-7}$	$9.5 \cdot 10^{-8}$	
2.33	2.50	22	0.997	$6.9 \cdot 10^{-7}$	$10.5 \cdot 10^{-8}$	
1.65	3.03	22	0.970	$21.9 \cdot 10^{-7}$	$33.4 \cdot 10^{-8}$	
0.87	3.72	22	0.981	$73.3 \cdot 10^{-7}$	$112 \cdot 10^{-8}$	
System D: $Me_3SiOSiMe_3 + ClC(O)OCH_2Me_2SiOSiMe_2CH_2O(O)CCl$						
2.45	2.05	17	0.996	$5.5 \cdot 10^{-5}$	$1.01 \cdot 10^{-5}$	5.5

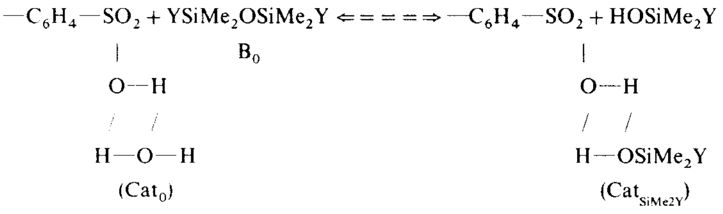
rate constants on the type of substituents (X and Y) at silicon and on initial concentrations of starting symmetrical organodisiloxanes may be provided by reaction mechanism features.

At the interaction of organodisiloxanes with reaction centers of the catalysts two types of the intermediate centers are formed including fragments of any either siloxane:



$$-C_6H_4-SO_2 + \underset{A_0}{XSiMe_2OSiMe_2X} \Leftarrow\!=\!=\!=\!=\!\Rightarrow -C_6H_4-SO_2 + HOSiMe_2X \quad (1.9)$$

$$\underset{(Cat_0)}{\begin{array}{c} | \\ O-H \\ /\;\;/ \\ H-O-H \end{array}} \qquad\qquad \underset{(Cat_{SiMe2X})}{\begin{array}{c} | \\ O-H \\ /\;\;/ \\ H-OSiMe_2X \end{array}}$$



$$\begin{array}{ccccc} -C_6H_4-SO_2 & + YSiMe_2OSiMe_2Y & \Leftarrow===\Rightarrow & -C_6H_4-SO_2 & + HOSiMe_2Y \\ | & B_0 & & | & \\ O-H & & & O-H & \\ / \quad / & & & / \quad / & \\ H-O-H & & & H-OSiMe_2Y & \\ (Cat_0) & & & (Cat_{SiMe2Y}) & \end{array} \quad (1.10)$$

Since dehydrated "KU-23" sulphocationite is unsuitable as catalyst of redistribution reaction, water participation in the formation of active centers is indispensable and it is consistent with previously obtained data upon water activation effects in the case of acidic catalysis [15]. Amount of active reaction centers of both forms is constant, it is determined by initial concentration of starting components —M_0, L_0, Cat_0. Formation of asymetrical organodisiloxanes doesn't change content of the reaction centers because they interact with catalyst resulting in formation of the same centers. The reaction centers may interact with component of reaction mixture according to equations (1.11) and (1.12):

$$Cat-SiMe_2X + YSiMe_2OSiMe_2Y \Leftarrow==\Rightarrow Cat-SiMe_2Y + YSiMe_2OSiMe_2X \quad (1.11)$$

$$Cat-iMe_2Y + XSiMe_2OSiMe_2X \Leftarrow==\Rightarrow Cat-SiMe_2X + YSiMe_2OSiMe_2X \quad (1.12)$$

Taking into account the availability of two types of the reaction centers and two types of reagents it is believed that observed decreasing of the rate constant values at reagent ratio change is determined by the interaction of less active substance with reaction center as a principal stage.

2.2. Investigation of Disproportionation Process of Oligoethoxysiloxanes

A great number of works [16–29] is devoted to the investigations on reaction of hydrolytic polycondensation of tetraethoxysilane (TES) in the presence of acidic and alkaline catalysts. In the case of alkaline hydrolysis NaOH, KF, NH_3 are used as catalysts, at acidic hydrolysis – inorganic acids: HCl, HNO_3, H_3PO_4 [20, 22–27]. It is supposed that hydrolysis process of TES, catalyzed by acids consists in a series of successive and parallel stages involving the hydrolysis reactions as well as inter-and intramolecular homofunctional condensation of $\equiv$Si—OH and $\equiv$Si—O—Et groups. As a result of reaction at partial hydrolysis linear and cyclic ethoxysiloxanes are formed and at complete hydrolysis – silicon dioxide [20]. However, description of the process in above mentioned works has mainly qualitative character. In work [26] the dependence of TES, hexaethoxydisiloxane (L_2) and octaethoxytrisiloxane (L_3) contents at change of H_2O : TES molar ratio from 0 up to 1 is described. Under examination of these results it follows that composition of the products is considerably different from the statistic one that could be obtained at polycondensation of tetrafunctional compounds [30]. The present investigation evaluation on disproportionation of model individual oligoethoxysiloxanes L_2 and L_3 has been carried out, they correspond to reactions:

$$2(EtO)_4Si + H_2O = = = = = \Rightarrow Et[OSi(OEt)_2]_2OEt + 2EtOH \qquad (2.1)$$

$$3(EtO)_4Si + 2H_2O = = = = = \Rightarrow Et[OSi(OEt)_2]_3OEt + 4EtOH \qquad (2.2)$$

The investigation was conducted by GLC method through determination of ethoxysiloxane contents with number of silicon atoms over 1 to 5. The disproportionation of ethoxysiloxanes may be presented by equation:

$$\begin{aligned} & q_nEt[OSi(OEt)_2]_nOET = = = = \Rightarrow (EtO)_4Si \\ & \quad + q_{n-1}Et[OSi(OEt)_2]_{n-1}OEt \\ & \quad + q_{n+1}Et[OSi(OEt)_2]_{n+1}OEt + q_iEt[OSi(OEt)_2]_iOEt \qquad (2.3) \end{aligned}$$

where $q_1 \cdots q_i$ – molar ethoxysiloxane concentrations with silicon atom number from 1 to 5.

The composition of ethoxysiloxanes disporportionation could be given by statistic Flory equation indicating the product contents with various molecular mass at polyfunctional monomers polycondensation [30].

$$q_i = \frac{(f_i - i)!f}{(i-1)!(f_i - 2i + 2)!i} \cdot P^{(i-1)} \cdot (1 - P)^{(fi - 2i + 2)} q_{no} \qquad (2.4)$$

where i – a number of silicon atoms in molecule; $f=4$; $P=0.25$ for L_2 and 0.33 for L_3; q_n – number of starting reagent moles.

The disproportionation reaction was carried out with the use of nucleophilic catalysts: L_2 – in the presence of KF, Me_4NOH, Me_4NF, L_3 – in the presence of KF and Me_4NOH. To determine equilibrium composition and disproportionation process rate – reaction temperature dependence in the presence of Me_3SiONa and Me_4NOH was studied. The disproportionation reaction rate depends on catalyst nature and reaction temperature. Thus, L_2 disproportionation in the presence of KF proceeded with remarkable rate at temperature over 150 °C, that is why the reaction was studied at 160 °C. As a result of disproportionation reaction formation of TES, L_3, decaethoxytetrasiloxane (L_4) and decreasing of L_3 concentration (Tab. 2.1) were observed. System reaches the equilibrium after 9.5 hr. Time of the equilibrium to be reached was determined versus time the equilibrium reached by TES, because with TES the constant concentration is reached much slower. Disproportionation in the presence Me_4NOH proceeds even at room temperature (19 °C). In the presence of this catalyst even at 19 °C the reaction rate is well above that in the case of KF. The equilibrium is reached within 3 hrs with obtaining of similar products. Time of equilibrium reaching is reduced and at 100 °C accounts for 2 min. In the presence of Me_3SiONa the disproportionation begins at 35 °C and at 108 °C the rate increases five times and time of equilibrium achievement accounts for 35 min.

Effect of Me_4NF in contrast to above catalysts is characterized by given prolonged induction period. In the process of heating at 100 °C the reaction begins within 1.5 hr and then is accompanied by rather sharp increasing of the rate, and the equilibrium is reached within 5.5 hr including the induction period. The disproportionation reaction of L_3 in the presence of KF at 160 °C proceeds much slower than in the case of L_2 and the equilibrium is reached in about 11 hr. In the equilibrium state a system already contains five components: TES, L_2, L_3, L_4 and dodecaethoxypentasiloxane (L_5); the latter appears within 5 hrs after the reaction begins. The process of L_3 disproportionation in the presence of Me_4NOH undergoes conversions similarly to L_2 even at 19 °C but much slower than for L_2. For L_3 the equilibrium is reached within 3.5 hr and the system contains the same five components. As in the case of L_2 the process rate in the presence of Me_4NOH is higher than in the presence of

TABLE 2.1 Equilibrium composition of disproportionation reaction products of oligoethoxysiloxanes ($[L_2]_0 = 2.3$ mol/l (at use of KF, Me_4NOH, Me_4NF) and 1.68 mol/l (Me_3SiONa); $[L_3]_0 = 1.25$ (KF) and 1.36 mol/l (Me_4NOH)

Components	*Component contents in reaction mixture, mol/l*										
	Disproportionation of $Et[OSi(OEt)_2]_2OEt$										
	KF	*Me_4NOH*				*Me_4NF*	*Esti-mated*	*Me_3SiONa*			*Esti-mated*
	160°	19°	40°	60°	100°	100°		35°	70°	108°	
$Si(OEt)_4$	1.41	1.46	1.43	1.48	1.50	1.52	1.52	1.06	1.06	1.06	1.07
$Et[OSi(OEt)_2)_2OEt$	0.42	0.43	0.42	0.42	0.41	0.42	0.41	0.30	0.32	0.32	0.31
$Et[OSi(OEt)_2)_3OEt$	0.20	0.20	0.21	0.20	0.19	0.18	0.18	0.13	0.13	0.13	0.13
$Et[OSi(OEt)_2)_4OEt$	0.09	0.09	0.10	0.09	0.08	0.09	0.09	0.06	0.07	0.07	0.07
$Et[OSi(OEt)_2)_5OEt$	–	–	–	–	–	–	–	–	–	–	–
	Disproportionation of $Et[OSi(OEt)_2]_3OEt$										
	KF			*Estimated*		*Me_4NOH*			*Estimated*		
	160°C			–		19°			–		
$Si(OEt)_4$	0.71			0.74		0.81			0.81		
$Et[OSi(OEt)_2)_2OEt$	0.31			0.22		0.24			0.24		
$Et[OSi(OEt)_2)_3OEt$	0.10			0.10		0.10			0.11		
$Et[OSi(OEt)_2)_4OEt$	0.09			0.05		0.06			0.06		
$Et[OSi(OEt)_2)_5OEt$	0.032			0.033		0.034			0.035		

KF. The equilibrium concentrations found experimentally are in agreement with those estimated from the formula (2.4) (Tab. 2.1) within the range of experiment error. The activity of used catalysts in the disproportionation reaction is diminished in a series $Me_4NOH > Me_3SiONa > Me_4NF > KF$. In the presence of Me_4NOH and Me_3SiONa disproportionation reaction proceeds as follows:

$$\equiv\mathrm{SiOEt} + \mathrm{MX} \Leftarrow = = = \Rightarrow \equiv\mathrm{Si{-}O{-}M} + \mathrm{EtX} \qquad (2.5)$$

$$\equiv\mathrm{Si{-}O{-}M} + \mathrm{Et[OSi(OEt)_2]_mOET}$$

$$\Leftarrow = \Rightarrow \equiv\mathrm{OSi{-}O{-}Et} + \mathrm{MO[Si(OEt)_2O]_mEt} \qquad (2.6)$$

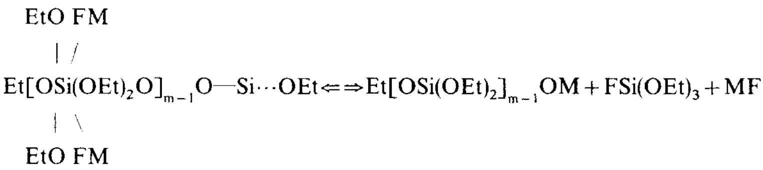
$$\mathrm{Et[OSi(OEt)_2]_mOM} + \mathrm{EtO(Si(OEt)_2O]_mEt} \Leftarrow = = = = = = \Rightarrow$$

$$\mathrm{EtO[Si(OEt)_2O]_{m+q}Et} + \mathrm{Et[OSi(OEt)_2]_{m-q}OM} \qquad (2.7)$$

where $M = Me_4N$, Na; $X = OH$, $OSiMe_3$.

In the presence of Me_4NF and KF the following scheme by analogy with other reactions catalyzed by fluorides [31] may be suggested:

$$\mathrm{Et[OSi(OEt)_2]_{m-1}OSi(OEt)_3} + 2\mathrm{MF} \Leftarrow = = = = = \Rightarrow$$



$$\mathrm{Et[OSi(OEt)_2O]_{m-1}O{-}}\underset{\underset{\mathrm{EtO\ FM}}{|\ \backslash}}{\overset{\overset{\mathrm{EtO\ FM}}{|\ /}}{\mathrm{Si}}}\cdots\mathrm{OEt} \Leftarrow\Rightarrow \mathrm{Et[OSi(OEt)_2]_{m-1}OM} + \mathrm{FSi(OEt)_3} + \mathrm{MF}$$

(2.8)

$$\mathrm{Et[OSi(OEt)_2]_{m-1}OM} + \mathrm{Et[OSi(OEt)_2]_mOEt} \Leftarrow = = \Rightarrow$$

$$\mathrm{Et[OSi(OEt)_2]_{m+q}OEt} + \mathrm{Et[OSi(OEt)_2]_{m-q}OM} \qquad (2.9)$$

where $M = Me_4N$, K.

The disproportionation reaction proceeds at the expense of ethoxysiloxanes redistribution at interaction with nucleophilic catalysts upon $\equiv$Si—O bond in the fragments $\equiv$Si—O—Si$\equiv$ and $\equiv$OSi—O—Et. For compounds under study the disproportionation reactions running up to the equilibrium reaching may be described in general manner with use of the system of reversible reactions. Thus, at L_2 disproportionation the formation of all products in accordance with equilibrium composition may be presented by three principal equations

$$\underset{A}{2Et[OSi(OEt)_2]_2OEt} \overset{K_1}{\Leftarrow\!=\!=\!=\!=\!\Rightarrow} \underset{B}{(EtO)_4Si} + \underset{C}{Et[OSi(OEt)_2]_3OEt} \quad (2.10)$$

$$A + C \overset{K_2}{\Leftarrow\!=\!=\!=\!=\!=\!=\!\Rightarrow} B + \underset{D}{Et[OSi(OEt)_2]_4OEt} \quad (2.11)$$

$$A + D \overset{K_4}{\Leftarrow\!=\!=\!=\!=\!=\!=\!=\!\Rightarrow} 2C \quad (2.12)$$

These equations comply with equilibrium constants K_1, K_2, K_4 that may be estimated from formula:

$$K_1 = \frac{[C][B]}{[A]^2}(2.13);\; K_2 = \frac{[B][D]}{[A][C]}(2.14);\; K_4 = \frac{[C]^2}{[A][D]} \quad (2.15)$$

In the case of L_3 disproportionation to foregoing equations three more can be added

$$A + D \overset{K_3}{\Leftarrow\!=\!=\!=\!=\!\Rightarrow} B + \underset{E}{Et[OSi(OEt)_2]_5OEt} \quad (2.16)$$

$$A + E \overset{K_5}{\Leftarrow\!=\!=\!=\!=\!\Rightarrow} C + D \quad (2.17)$$

$$C + E \overset{K_6}{\Leftarrow\!=\!=\!=\!=\!=\!\Rightarrow} 2D \quad (2.18)$$

the following equilibrium constants correspond to them

$$K_3 = \frac{[B][E]}{[A][D]}(2.19);\; K_5 = \frac{[C][D]}{[A][E]}(2.20);\; K_6 = \frac{[D]^2}{[C][E]} \quad (2.21)$$

As may be seen from Table 2.2 statistical equilibrium constant calculated from formulas (2.13–2.15) and (2.19–2.21) with the use of the equilibrium concentrations calculated from equation (2.4) and equilibrium constants obtained experimentally agree within the limits of experiment error.

Equality of these constants indicates that disproportionation reactions of oligoethoxysiloxanes follow Flory statistical theory. It is evident from Tables 2.1 and 2.2 that values of equilibrium concentrations and equilibrium constant remain valid at various temperatures. Enthalpy of equilibrium reactions under consideration is practically equal to zero and the equilibrium is completely statistical.

The investigation on the disproportionation reactions in the presence of HCl, H_3PO_4, HNO_3 showed that these acids couldn't catalyze the processes of disproportionation of oligoethoxysiloxanes. On the base of obtained results the conclusion may be made that during the process of hydrolytic TES condensation, the presence of nucleophilic reagents may influence the disproportionation reaction of formed oligoethoxysiloxanes. At catalysis of hydrolytic polycondensation by acids the disproportionation reaction mustn't markedly influence product composition since it isn't catalyzed by acids.

The disproportionation of products of hydrolytic polycondensation of TES obtained at different values of molar $n = [H_2O]_0 : [TES]_0$ ratio.

$$q_1(EtO)_4Si + nq_1H_2O = = = = q_iEt[OSi(OEt)_2]_{m-1}OEt + 2nq_1 EtOH \quad (2.22)$$

Study of composition of obtained products and reaction rate at products disproportionation with a different extent of TES polycondensation and correlation of this process with a disproportionation of individual ethoxysiloxanes has been conducted.

In the process of TES hydrolytic polycondensation at different "n" linear and cyclic ethoxysiloxanes are formed and linear ethoxysiloxane contents is statistical, estimated from Flory equation (2.4), where x – number of silicon atoms in molecule of linear ethoxysiloxanes, $f = 4$, $P = n/2$, q_0 – initial TES concentration. This derivation was attributed to the absence of equilibrium reactions at hydrolytic polycondensation and formation of ethoxysiloxanes that is disregarded by Flory theory. The products of TES polycondensation, obtained at ratios of $n = 0.2–1.2$ in the presence of 0.005 mol/l HCl were chosen as starting oligoethoxysiloxanes for study of disproportionation.

TABLE 2.2 Equilibrium constants of disproportionation reaction of oligoethoxysiloxanes

Equilibrium constant	*Statistical constant*	*Average value of contants*	*Experimental constant of equilibrium*									
			Disproportionation of $Et[OSi(OEt)_2]_2OEt$								*Disproportionation of* $Et[OSi(OEt)_2]_3OEt$	
			KF	Me_4NOH			Me_4NF	Me_3SiONa			*KF*	Me_4NOH
			100°*C*	19°	60°	100°	100°	35°	70°	108°	160°	19°
K_1	1.56	1.52	1.54	1.51	1.51	1.51	1.61	1.53	1.49	1.49	1.50	1.49
K_2	1.76	1.74	1.59	1.69	1.68	1.78	1.78	1.71	1.81	1.79	1.81	1.79
K_3	2.06	2.03	–	–	–	–	–	–	–	–	2.01	2.04
K_4	0.89	0.90	0.92	0.90	0.99	0.94	0.91	0.94	0.79	0.84	0.84	0.79
K_5	0.73	0.66	–	–	–	–	–	–	–	–	0.64	0.68
K_6	0.89	0.90	–	–	–	–	–	–	–	–	0.92	0.88

The disproportionation was carried -out in the presence of Me_4NOH in amount of 0.01 mol/l at 20 °C. The process running is controlled by GLC method through determination of content of TES and ethoxysiloxanes with number of silicon atoms from 2 to 5. For products of hydrolytic TES polycondensation, obtained at different "n" values the disproportionation is characterized by TES concentration increasing and its formation in that products wherein it was absent, by L_2, L_4 and L_5 appearing in the products wherein they are absent and L_2, L_3, L_4 and L_5 redistribution finally. At the disproportionation of product of hydrolytic TES polycondensation, obtained at $n = 0.2$ TES concentration increases from 1.4 up to 1.5 mol/l with simultaneous decreasing of L_2 and L_3 content (from 0.3 to 0.25 and from 0.1 to 0.06 mol/l, respectively. At the same time L_4 and L_5 formation is observed with concentration increasing from 0.02 and 0.006 mol/l respectively. In the case of disproportionation of hydrolytic polycondensation products obtained at $n = 1.2$ TES L_2 and L_4 are formed with concentration increasing up to 0.06; 0.01 and 0.001 mol/l, respectively. Content of L_3 and L_5 is diminished from 0.03 up to 0.003 and from 0.01 up to 0.0004 mol/l, respectively. With n rise the time of reaction system transition into equilibrium state (from 2 hr at $n = 0.2$ to 24 hr at $n = 1.2$) is also increased, that is more likely connected with activity change of ammonium catalysts at growth of OH-group content (from 0 to $n = 0.2$ up to 27% at $n = 1.2$) because it is known [32] that activity of tetra-alkylammonium catalysts is reduced in the presence of hydroxyl containing compounds. This is also supported by that the time of equilibrium acheived in the process of disproportionation of the product of TES hydrolytic polycondensation at $n = 1.0$ in which OH-groups were preliminary condensed is reduced by two times. In all instances equilibrium composition found experimentally in accordance with composition calculated from formula (2.4). In this way the process of disproportionation of products of TES hydrolytic polycondensation is not different from the disproportionation of individual ethoxysiloxanes. As a result of the disproportionation, the consumption also takes place up to full exhausting of cyclic ethoxysiloxanes: hexaethoxycyclotrisiloxane (S_3), octaethoxycyclotetrasiloxane (S_4), decaethoxycyclopentasiloxane (S_5), which enter into reactions of polymerization and disproportionation. This is demonstrated in the example of S_4 that in ethanol medium and in the presence of ammonia (ammonia doesn't cause the ethoxysiloxane disproportionation) at room temperature is polymerized up to 100% conversion without formation of low molecular ethoxysiloxanes. Reaction rate adheres to the equation of the first order with constant rate of $1{,}85.10^{-4}s^{-1}$. In the absence of alcohol NH_3 doesn't cause polymerization that is why it may be believed that at interaction with alcohol it gives ammonium base:

$$NH_3 + EtOH \Leftarrow = = = = = = = \Rightarrow EtONH_4 \quad (2.23)$$

which leads to polymerization according to scheme (2.24, 2.25).

$$m[(EtO)_2SiO]_4 + EtONH_4 \Leftarrow = = = = = = = \Rightarrow EtO[(EtO)_2SiO]_4NH_4 \quad (2.24)$$

$$EtO[(EtO)_2SiO]_4NH_4 \Leftarrow = = = = = = = \Rightarrow EtO[(EtO)_2SiO]_4H + NH_3 \quad (2.25)$$

In the presence of 0,01 mol/l of Me_4NOH in amount 0,01 mol/l of S_4 enteres immediately into disproportionation reaction with formation TES and linear ethoxysiloxanes. Content of TES and linear ethoxysiloxanes with numbering of silicon atoms from two up to five also corresponds to the statistical estimated from formula (2.4) at $P = 0{,}5$ equal in conversion. At initial S_4 concentration 1 mol/l 0.4(0.38) mol/l TES was formed; 0.11 (0.095) mol/l L_2, 0.04(0.035) mol/l L_3; 0.01(0.016) mol/l L_4; 0.007(0.008) mol/l L_5.

Equilibrium diethoxycyclosiloxanes concentration is near to the zero. However this doesn't exlude a possibility of cyclic fragment content in the formed polymeric chain.

2.3. Characteristic Properties of Cooligomerization of Dimethylcyclosiloxanes with Tetraethoxysilane at catalysis with Nucleophilic Reagents

The reactions of organosiloxanes with organoalkoxysilanes of different functionality and tetraalkoxysilanes catalyzed by nucleophilic and electrophilic reagents and proceeding with redistribution of alkoxy-groups and siloxane bonds are of interest for direct synthesis of a variety of monomeric and oligomeric compounds [33–37]. These reactions permit us to change over a wide range the product compositions versus the organoalkoxysilane functionality, substituent nature at silicon, reagent ratios, catalyst and conditions of reaction performing.

The present investigation deals with study of features of cooligomerization of TES with D_3 and octamethylcyclotetrasiloxane (D_4), catalyzed by nucleophilic reagents: polydimethylsiloxane-α,ω-diolate tetramethyl ammonium (TMAS), KOH and Me_4NOH (TMAH). At the D_3 interaction with equimolar TES quantities in the presence of TMAS ($[D_3]_0 = [TES]_0 = 0.6$; $[TMAS]_0 = 0.0017$ mol/l) over temperature range 20–40 °C D_3 is consumed rather faster than TES. Thus if D_3 is fully consumed in 15 min (at 20 °C), TES is consumed at the same time by 25%. The higher rates of D_3 consumption are possible due to telomerization involving the interaction upon some TES ethoxygroups and extending of dimethylsiloxane chain

$$a\,Si(Oet)_4 + mn[Me_2SiO]_3 \overset{Cat.}{\Longleftarrow\!=\!=\!=\!=\!=\!\Longrightarrow} (EtO)_{4-m}Si[(OSiMe_2)_{pn}OEt]_m \quad (3.1)$$

where p = 3, 4; m = 1–4.

Consumption of D_3 is of the first order according to given concentration D_3

$$W_D = -k_D[D_n] \quad (3.2)$$

and for TES – the second summable total order according to given concentration of D_3 and TES

$$W_{TES} = -k_{TES}[D_n][TES] \quad (3.3)$$

Values of effective k_{D3} and k_{TES} constants are presented in Table 3.1. The obtained relationships confirmed the assumption of D_3 and TES consumption from equation (3.1) in accordance to which the consumption rate of D_3 is dependent only on given concentration of D_3. On the exposure of the reaction mixture under given conditions after consuming of D_3 the formation 0.067 mol of dimethyldiethoxysilane (DMDS) per 1 mol of taken TES was observed. Formation of DMDS and simultaneous slight decreasing of TES concentration demonstrate the TES interaction with telomerization products upon terminal ethoxydimethylsiloxy group. However, DMDS low concentration and some change in TES concentration allows to conclude that the product compositions is little affected by this reaction. The major products are tetrafunctional compounds, forming according to equation (3.1). At 100 °C D_3 enters into

TABLE 3.1 Constants of D_3 and TES consumption rates at their cooligomerization catalyzed by TMAS ($[D_3] = [TES]_0 = 0.6$; $[TMAS]_0 = 0.0017$ mol/l)

$t, °C$	$k_D \cdot 10^4 s^{-1}$	$k_{TES} \cdot 10^4 s^{-1}$	$[DMDS]$, l/mol
21	5.6	2.0	0.020
28	3.4	4.4	0.025
30	7.5	5.3	0.027
40	56.7	12.7	0.040

reaction within 1–2 min at concentration twice as much than of TES ($[D_3]_0 = 1.2$; $[TES]_0 = 0.6$; $[TMAS]_0 = 0.0017$ mol/l); TES is consumed much lower and reaction rate is independent of given D_3 concentration since TES is consumed after D_3 vanishing. In this occasion D_3 consumption rate is described by the equation (3.2). For TES reaction order is changed in comparison with the process at temperatures 20–40 °C. The reaction rate is presented by the equation of the first order according to given TES concentration

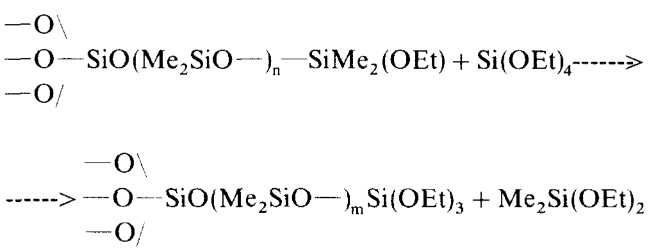
$$W_{TES} = -k''_{TES}[TES] \tag{3.4}$$

This allows to make assumption that in this case TES is actively consumed not only through interaction with D_3 but as well as with linear siloxane fragments of the products obtained according to the equation (3.1)

$$(\sim Me_2SiO \sim)_x + Si(OEt)_4 \overset{Cat.}{\Longleftrightarrow} (\sim Me_2SiO —)_{x-z} Et + (EtO)_3Si(OSiMe_2 \sim)_z \tag{3.5}$$

In contrast to D_3 at D_4 interaction with TES catalyzed by TMAS or TMAH $[D_4]_0 = 1.8$, $[TES]_0 = 1.2$; $[TMAS]_0 = 0.0017$ or $[TMAH]_0 = 0.0034$ mol/l at 80 °C coreagents are completely and simultaneously consumed. Consumption rate of D_4 and TES are presented by the equations of the first order (3.2) and (3.4), respectively. From this it follows that at D_4 interaction with TES the reagents consumption proceeds at the expense of reactions, described by the equations (3.1) and (3.5). Close values of effective consumption rate constants of D_4 and TES show that the reactivity of Si—O bond in siloxanes and TES is identical.

The comparison of polymerization processes of D_3 and D_4 and their cooligomerization with TES, catalyzed by TMAS shows that in the presence of TES the catalytic activity of TMAS towards to D_3 decreases and increases towards to D_4. Thus, if on D_3 polymerization at 40 °C ($[D_3]_0 = 0.6$; $[TMAS]_0 = 0.0017$ mol/l) a value of effective constant $k_D = 10.9 \cdot 10^{-3} sec^{-1}$. on D_4 polymerization at 80 °C($[D_4]_0 = 1.8$; $[TMAS]_0 = 0.0017$ mol/l) a value of $k_D = 4.72 \cdot 10^{-5} sec^{-1}$ and on introduction of 1.2 mol/l TES it increases up to 68, $5 \cdot 10^{-5} sec^{-1}$. At TES interaction with D_3 in the presence and with D_4 in the presence of TMAS or TMAH at 80–100°C the formation of large quantities of DMDS and tetramethyldiethoxydisiloxane (TMDDS) was observed at the expense of redistribution of ethoxy group and siloxane bonds in telomerization products (formed according to the equation (3.1)) or their interaction with TES according to the equation (3.5). Thus, in reaction of D_4 with TES the content of DMDS amounted to 0.45 mol/l, TMDDS – 0.27 mol/l at 100 °C, 0.4 and 0.18 mol/l at 90 °C, 0.26 and 0.18 mol/l at 80 °C, respectively that is the same as the participation of 30, 26 and 20% ethoxy groups, introduced with TES ($[D_4]_0 = 1.8$, $[TES]_0 = 1.2$; $[TMAS]_0 = 0.0017$ mol/l). During the reaction proceeding the TMDDS increases gradually and DMDS passes the maximum: 0.53 mol/l at 100 °C, 0.45 mol/l at 90 °C and 0.32 mol/l at 90 °C and 0.32 mol/l at 80 °C. Higher rates of content growth of DMDS than of TMDDS and its concentration passing the maximum allows to suppose that DMDS is predominantly produced at the expense of TES interacton with end ethoxydimethylsiloxy group of telomerization products:



$$\begin{array}{l} -O\backslash \\ -O-SiO(Me_2SiO-)_n-SiMe_2(OEt) + Si(OEt)_4\text{------}> \\ -O/ \\ \qquad -O\backslash \\ \text{------}> -O-SiO(Me_2SiO-)_mSi(OEt)_3 + Me_2Si(OEt)_2 \\ \qquad -O/ \end{array} \tag{3.6}$$

This leads to possible formation of DMDS under the reaction running in the quantity more than equilibrium one. At the expense of the subsequent reactions of ethoxy groups and siloxane bonds redistribution with DMDS participation the decreasing of its concentration takes place after passing the maximum up to the equilibrium. As is seen on the base of obtained results at the TES interaction with D_3 and D_4 in the presence of TMAS and TMAH the functionality (active ethoxy group contents) of reaction products could change from 2 up to 6 and over at the average functionality of four. At D_4 interaction with TES in the presence of KOH ($[D_4]_0 = 1.8$, $[TES]_0 = 1.2$; $[KOH]_0 = 0.1$ mol/l) consumption of the reagents is observed with marked rates at 140 °C and over. TES enters into reaction considerably faster than D_4. When TES enters almost completely into reaction D_4 is consumed only by 30% (140 °C). However D_4 consumption is continued and after TES vanishing up to fully exhausting. Fast consumption of TES at low D_4 consumption demonstrates that telomerization rate according to the equation (3.1) is much below that of epoxy groups and siloxane bonds redistribution at the expense of telomerization products interaction with TES according to the equations (3.5) and (3.6). The conversion depth by D_4 increases up to 70% by the moment of full TES exhausting at increasing of TES concentration from 1.2 up to 2.2 mol/l and D_4 concentration decreasing from 1.8 to 1.2 mol/l. In reactions catalyzed by KOH the formation of DMDS and TMDDS is also observed, They consist of 0.35 (maximum 0.40) and 0.12 mol/l at $[D_4]_0 = 1.8$, $[TES]_0 = 1.2$ mol/l as well as 0.9 (maximum 1.0) and 0.14 mol/l at $[D_4]_0 = 1.2$, $[TES]_0 = 2.2$ mol/l, respectively. The ethoxy group consumption introduced with TES for formation DMDS and TMDDS accounts for 26% of total quantity. The comparison of D_4 consumption with amount of dimethylsiloxy groups spent for DMDS and TMDDS formation shows that at the initial stage of the reaction a high destruction of the telomerization products proceeds with formation of predominantly DMDS and TMDDS. This is supported by hexaethoxydisiloxane formation as a result of limiting destruction of the telomerization products. At the prolonged reaction times when D_4 is practically vanished, decreases of DMDS and TMDDS content to the equilibrium level is observed. Noted features of D_4 interaction with TES in the presence KOH are consistent with data given in [37]; wherein in the reaction between TES and D_4 in the presence of KOH (at distillation of produced DMDS and TMDDS) formation of silicon dioxide may occur, that is a limiting case of TES ethoxy groups use for the production of these products. In this manner, the conducted investigation indicates that for considered reactions of dimethylcyclosiloxanes with TES three types of processes may be pointed out: telomerization taking place at the initial stages; TES interaction with the telomerization products and redistribution of ethoxy groups and siloxane bonds in the products formed at the expense of the processes of two previous types. The contribution of these processes may be changed with activity changes of dimethylcyclosiloxane and catalyst, temperature and time of reaction. Thus, on use of highly active D_3 and TMAS as catalyst at temperatures over 20–40 °C telomerization process is predominant. At D_4 cooligomerization with TES in the presence of KOH at 140 °C and higher at the intial reaction stage the processes of cleavage of telomerization products by tetraethoxysilane are dominant. In the case of TES cooligomerization with D_3 and D_4 in the presence of TMAS or TMAH at temperature over 80–100 °C all the processes under consideration proceed at high rates.

2.4. Investigation on the Regularities of Organosilsesquioxane Interactions with Tetraethoxysilane

The regularities of interaction of organosilsesquioxanes $(RSiO_{1.5})_n$ (T_n^R) where R = Me, Vi, Ph with tetraalkoxysilanes (TAS), tetramethoxysilane (TMS), tetraethoxysilane (TES) and tetrapropoxysilane (TPS) in the presence of nucleophilic catalyst-KOH have been investigated. During the reaction proceeding TAS interaction with T_n^R with redistribution of alkoxy groups and siloxane bonds takes place. The distribution of alkoxy groups and Si—O bonds between $Si(OR')_4$ and structural units $RSi(O—)_3$ may be presented by the equation

$$(R'O)_4Si + RSi(O-)_3 \overset{KOH}{\Longleftarrow\!=\!=\!=\!=\!\Longrightarrow} (-O)_aSi(R'O)_{4-a} + R(R'O)_BSi(O-)_{3-B} \qquad (4.1)$$

where "a" may be changed from 0 to 4 and b from 0 to 3.

The redistribution reaction may be presented the most simply as follows:

$$\equiv Si-OR' + =(R)Si^*-O- \Longleftarrow\!=\!=\!=\!=\!=\!\Longrightarrow -Si-O- + =(R)Si^*-O-R' \qquad (4.2)$$

where —Si – designated tetrafunctional and =(R)Si* – designated trifunctional units.

Due to the equilibrium character of the process the reaction products must contain the following tetra- and trifunctional units $(R'O)_4Si$(TAC), $(R'O)_3SiO$ (I), $(R'O)_2Si(O—)_2$ (II), $(R'O)Si(O—)_3$ (III), $Si(O—)_4$ (IV), $RSi(O—)_3$ (V), $R(R'O)Si(O—)_2$ (VI), $R(R'O)_2SiO$ (VII), and in the limiting case organotrialkoxysilanes- RSi $(OR')_3$ (VIII). The combination of units containing siloxane bond leads to formation of oligoalkoxysiloxanes of different composition and structure, they may be present only as brutto-formula displaying the content of different units. The reactions scheme with regard to formed monomeric and oligomeric products may be given as the following equation:

$$d[RSiO_{1,5}]_n + q(R'O)_4Si \overset{KOH}{\Longleftarrow\!=\!=\!=\!\Longrightarrow} cRSi(OR')_3 + Z[(R'O)_3SiO_{0,5}]_f$$

$$-[(R'O)_2SiO]_s[(R'O)SiO_{1,5}]_g[SiO_2]_m[(R'O)RSiO]_h[RSiO_{1,5}]_k$$

$$[R(R'O)_2SiO_{0,5}]_j + p(R'O)_4Si \qquad (5.3)$$

Organotrialkoxysilanes VIII were obtained in the pure state for their identification and quantitative determination in the reaction products, identification was carried out by methods of GLC, ^{29}Si, ^{13}C, ^{1}H NMR spectroscopy. Analysis of ^{29}Si NMR spectra of the starting compounds and reaction products at the different reagent ratios allowed to identify the signals applying to silicon atoms in TAS, units I–III, V–VII and RSi $(OR')_3$. Silicon signals for TAS and VII are singlet and for I–III and V–VII – widened complicated multiplets resulting from their inclusion into various types of structural fragments.

Chemical shifts of ^{29}Si signals do not significantly depend on alkyl group in alkoxy substituent and have the following values:

δ^{29}Si TAS 0(-78)-(-82) ppm; δ^{29}Si I(-85)-(-90) ppm;
δ^{29}Si II(-95)-(-97) ppm; δ^{29}Si III (-101)-(-105) ppm;
δ^{29}Si V(-67)-(-80) ppm; (R = Me); (-77)-(-85) ppm(R = Ph, Vi);
δ^{29}Si VI(-56)-(-60) ppm; (R = Me); (-71)-(-74) ppm(R = Ph, Vi);
δ^{29}Si VII(-45)-(-51) ppm;(R = Me); (-62)-(-67) ppm(R = Ph, Vi);
δ^{29}Si VIII(-38)-(-44) ppm;(R = Me); (-53)-(-58) ppm(R = Ph, Vi).

Integral intensity ratios of silicon signals for T_n^R and TAS in the initial mixture as well as integral intensity sum of TAS, tetrafunctional units

I–IV and for trifunctional units V–VIII in finished products correspond to the taken reaction mixture composition. Units IV and V were the most difficult to identify. Thus, IV could be identified in neither reaction product and V was identified only at molar ratio $[T_n^R]_0$: $[TAS]_0 =$ 1 : 0, 5. Good agreement of molar ratio of rated values for tetrafunctional and trifunctional units with experimentally found integral intensity ratios of ^{29}Si signals allowed to find out that ^{29}Si NMR can be used for quantitative determination of TAS, VIII, units I–III and V–VII in the reaction mixture with an accuracy of 10%. This also indicates the absence or low content of unit IV under chosen ratios of the reagents. Mole fraction of each unit was determined for TAS and I–IV on the base of ^{29}Si NMR spectra by a formula:

$$S'_n \Big/ \sum_{n=0}^{n=4} S'_n (n = 0 - 4) \tag{4.4}$$

and for V–VIII by a formula

$$S''_m \Big/ \sum_{m=0}^{m=3} S''_m \tag{4.5}$$

where S'_n – integral intensity of silicon signals for tetrafunctional units, S''_m – integral intensity of silicon signals for trifunctional units. It was proved by means of GLC method and by TAS and VII content change that on various TAS interaction with T_n^{Ph} at $[T_n^{Ph}]_0 = 0.33$ mol/l, $[TAS]_0 = 1$ mol/l, $[KOH]_0 = 0.008$ mol/L and $t = 70\,^\circ C$, TMS was the most reactive (65% conversion was achieved during 3 min), then follows TES (25 min). The growth of TAS reactivity as alkyl substituent content is decreased agrees well with nucleophilic character of the reaction and drop of alkyl group steric effect. The higher is TAS reactivity the more is $RSi(OR')_3$ formation rate. The reactivity of T_n^R with different "R" does not change significantly. Under the chosen ratio of reagents and after reaction of TAS with T_n^R in the equilibrium TAS content is 0.37–0.42 mol fr. (in regard of $[TAS]_0$ and VIII – 0.40–0.50 mol. fr. (in regard of $[T_n^R]_0$). On the ground of reaction product chromatography analysis for the content of $(R'O)_4Si$ and $RSi(OR')_3$ balanced amounts one can come to the conclusion that the nature of a substituent at silicon in T_n^R or alkoxy group does not greatly effect them. The study of T_n^R reaction with TAS at temperatures of 40, 50, 60 and 70 °C ($[T^R_n]_0 = 0.33$ mol/l, $[KOH]_0 = 0.008$ mol/l) proved that balanced content of TAS and VIII does not depend on temperature. It is demonstrated by the example of T^{Ph}_n reaction with TMS. On the ground of analysis of silicon signal integral intensity ratios in ^{29}Si NMR spectra by equation (4.4) and (4.5), equilibrium content in molar fraction of TAS, I–IV (in regard to $[TAS]_0$) and V–VIII (in regard to $[T^R_n]_0$ with $[T^R_n]_0$ and $[TAS]_0$ molar ratios (in terms of one unit) – 1 : 0.5; 1 : 1.5; 1 : 3; 1 : 4.5; 1 : 6 was found. With the purpose to find general regularities of alkoxy-group distributions by units experimental data comparison with possible statistic content of various units in the reaction product equilibrium mixture was carried out. Thus molar fractions of alkoxy-groups (a_0) related to intial TAS and siloxy-bonds (b_0) related to T^R_n were calculated in regard to total sum of reactive groups by formulas (4.6, 4.7)

$$a_0 = 4[TAC]_0 : (4[TAC]_0 + 3[T^R_n]_0) \tag{4.6}$$

$$b_0 = 1 - a_0 \tag{4.7}$$

The sum of molar fractions of R′O – groups and siloxy-bonds, participating in the exchange is assumed as 1. Equilibrium constant (K_e can be calculated on the ground of reaction equation (4.5) by formulas (4.8) and (4.9)

$$K_e \cdot a_e \cdot b_e = (a_0 - a_e)^2 \tag{4.8}$$

$$b_e = (1 + a_e - 2a_0),\ \text{TO}\ K_e = (a_0 - a_e)^2/(a_e)\cdot(1 - 2a_0 + a_e) \tag{4.9}$$

Where a_e is an equilibrium molar fraction of alkoxy – groups, related to tetrafunctional units, b_e – is an equilibrium molar fraction of siloxy-bonds, related to trifunctional units; a/a_0 ratio can be determined on the base of ^{29}Si signal integral intensities in NMR-spectra of equilibrium mixture by the following formulas

$$a_e/a_0 = \sum_{n=0}^{n=4} S'_n \Big/ \left(\sum_{n=0}^{n=4} S'_n + \sum_{m=0}^{m=4} S''_m \right) = y \tag{4.10}$$

$$\sum_{n=0}^{n=4} S'_n = 4S'_{TAC} + 3S'_I + 2S'_{II} + S'_{III} \tag{4.11}$$

where S'_{TAC}, S'_I, S'_{II} and S'_{III} are areas of silicon signals in tetrafunctional units, involving 4–1 ethoxy-groups at silicon respectively

$$\sum_{m=0}^{m=3} S''_m = 3S''_{VIII} + 2S''_{VII} + S''_{VI} \tag{4.12}$$

where S''_{VIII}, $2S''_{VII}$, S''_{VI} are areas of silicon signals in trifunctional uints, involving 3–1 ethoxy-groups at silicon. "K_e" value can be determined by formula (4.13)

$$\begin{aligned} K_e &= (a_0 - a_0y)^2/a_0y(1 + a_0y - 2a_0) \\ &= a_0(1 - y)^2/(y \cdot [1 - a_0(2 - y)]) \end{aligned} \tag{4.13}$$

It was found that "K_e" values for TAS reaction with T^R_n were equal to 1–0.1, i.e. functional group distributions between tetra- and tree functional units were proportional to molar fraction of the functional groups, related to these units and were statistic ones. Formulas of statistic distribution were used to determine equilibrium quantities of $[TAS]_e$, $[VIII]_e$ and units $[I]_e$–$[VI]_e$ at statistic content. The contents of each type units provided by tetrafunctional silicon atoms (in mol. fract.) can be calculated by the following equations

$$[TAC]_e = (a_e)^4/(a_0)^4 \tag{4.14}$$

$$[I]_e = 4(a_e)^3(a_0 - a_e)/(a_0)^4 \tag{4.15}$$

$$[II]_e = 6(a_e)^2(a_0 - a_e)^2 0/(a_0)^4 \tag{4.16}$$

$$[III]_e = 4(a_e)(a_0 - a_e)53\ 0/(a_0)^4 \tag{4.17}$$

$$[IV]_e = (a_0 - a_e)4/(a_0)^4 \tag{4.18}$$

The content of various types of trifunctional units can be calculated by the equations

$$[\mathrm{VIII}]_e = (a_0 - a_e)^3/(1 - a_0)^3 \tag{4.19}$$

$$[\mathrm{VIII}]_e = 3(a_0 - a_e)(1 - 2a_0 + a_e)/(1 - a_0)^3 \tag{4.20}$$

$$[\mathrm{VI}]_e = 3(a_0 - a_e)^2(1 - 2a_0 + a_e)^2/(1 - a_0)^3 \tag{4.21}$$

$$[\mathrm{V}]_e = (1 - 2a_0 + a_e)^3/(1 - a_0)^3 \tag{4.22}$$

Hence on the ground of equations (4.14–4.22) statistic equilibrium contents of all unit types were calculated. Change of calculated and experimental values of various type unit content in regard of reagent ratios are shown in Tables 4.1 and 4.2. On the ground of equation (4.9) and value of $K_e = 1$ follows $a_e = a_0^2$. Comparison of calculated and experimental data for tetrafunctional units (Tab. 4.2) demonstrated their good agreement on recording by both ^{29}Si NMR spectroscopy and GLC for TAS. Derivations are in the range of determination error. General regularity of treefunctional unit content change tends to decline from statistic data regarding organotrialkoxysilanes VIII and to increase regarding units VI, VII (Tab. 4.2). Derivations from the calculated data may result from insignificant equilibrium shift among trifunctional units towards mixed alkoxysiloxane units.

Thus, on the ground of ^{29}Si NMR spectroscopy it was found that on TAS interaction with T_n^R alkoxy-groups distribution between trifunctional and tetrafunctional units as well as various type tetrafunctional unit contents in equilibrium products of catalytic rearrangement were close to statistic one, but increased content of alkoxysilane units was typical for trifunctional ones.

The study of various unit equilibrium contents at temperature range of 40–70°C by ^{29}Si NMR spectroscopy shows that they do not depend on temperature (Tab. 4.1).

This agrees with GLC data and leads to the conclusion that enthalpy factor slightly effects equilibrium composition of catalytic rearrangement reaction on alkoxy group interaction with siloxane bond. Study of equilibrium composition of various type units, TAS and VIII on TAS interaction with T_n^R demonstrates that enthalpy factor slight dependence

TABLE 4.1 Unit equilibrium contents during TMS reaction with T_n^{Me}(1–4), T_n^{Vi}(5–8) and T_n^{Ph}(9–12), TPS with T_n^{Me}(13–15), T_n^{Ph}(16–18) at various temperatures and theoretically calculated ones (19) at initial reagent ratios $[T_n^R]_0$: $[TAS]_0 = 1:3$

N	t°C	a_0	$[TAC]_0$	$[I]_e$	$[II]_e$	$[III]_e$	$[IV]_e$	$[V]_e$	$[VI]_e$	$[VII]_e$	$[VIII]_e$
1	70	0.80	0.38	0.45	0.15	0.02	–	–	0.12	0.43	0.45
2	60	0.80	0.39	0.47	0.13	0.01	–	–	0.10	0.45	0.44
3	50	0.80	0.38	0.45	0.16	0.01	–	–	0.12	0.44	0.44
4	40	0.80	0.37	0.47	0.16	–	–	–	0.11	0.44	0.45
5	70	0.80	0.36	0.46	0.15	0.03	–	–	0.14	0.44	0.42
6	60	0.80	0.35	0.47	0.18	–	–	–	0.12	0.46	0.42
7	50	0.80	0.35	0.46	0.19	–	–	–	0.17	0.45	0.38
8	40	0.80	0.37	0.47	0.16	–	–	–	0.12	0.44	0.44
9	70	0.80	0.34	0.47	0.19	–	–	–	0.06	0.47	0.47
10	60	0.80	0.35	0.48	0.17	–	–	–	0.15	0.46	0.39
11	50	0.80	0.36	0.47	0.17	–	–	–	0.17	0.44	0.41
12	40	0.80	0.37	0.46	0.16	–	–	–	0.21	0.44	0.35
13	70	0.80	0.41	0.46	0.13	–	–	–	0.19	0.48	0.33
14	60	0.80	0.37	0.45	0.18	–	–	–	0.21	0.47	0.32
15	50	0.80	0.39	0.45	0.16	–	–	–	0.17	0.46	0.37
16	70	0.80	0.38	0.47	0.15	–	–	–	0.12	0.48	0.40
17	60	0.80	0.38	0.47	0.15	–	–	–	0.13	0.49	0.38
18	50	0.80	0.38	0.46	0.16	–	–	–	0.13	0.44	0.43
19	–	0.80	0.41	0.46	0.15	0.03	$1\cdot10^{-4}$	$8\cdot10^{-3}$	0.10	0.38	0.51

TABLE 4.2 Equilibrium unit contents on T_n^{Me} reaction with TES (1, 4, 12, 20) and TPS (5, 13, 21), T_n^{Ph} with TMS (6, 14, 22), TES (2, 7, 15, 23) and TPS (8, 16, 24), T_n^{Vi} with TMS (9, 17, 25) and TES (10, 18, 26) and theoretically calculated ones (3, 11, 19, 27)

N	*t*° *C*	a_0	$[TAC]_0$	$[I]_e$	$[II]_e$	$[III]_e$	$[IV]_e$	$[V]_e$	$[VI]_e$	$[VII]_e$	$[VIII]_e$
1	70	0.40	0.05	0.13	0.35	0.47	–	0.27	0.43	0.25	0.25
2	70	0.40	0.04	0.12	0.38	0.46	–	0.26	0.45	0.23	0.06
3	–	0.40	0.03	0.15	0.35	0.35	0.13	0.22	0.43	0.29	0.06
4	70	0.67	0.18	0.40	0.26	0.16	–	–	0.32	0.48	0.20
5	70	0.67	0.22	0.47	0.31	–	–	–	0.29	0.51	0.20
6	70	0.67	0.14	0.39	0.33	0.14	–	–	0.23	0.50	0.27
7	70	0.67	0.15	0.34	0.33	0.18	–	–	0.27	0.51	0.22
8	70	0.67	0.18	0.42	0.30	0.10	–	–	0.28	0.51	0.21
9	70	0.67	0.17	0.42	0.30	0.11	–	–	0.25	0.49	0.26
10	70	0.67	0.17	0.40	0.35	0.08	–	–	0.24	0.55	0.21
11	–	0.67	0.20	0.40	0.29	0.10	–	–	0.22	0.44	0.30
12	70	0.86	0.49	0.38	0.13	–	–	–	0.22	0.39	0.39
13	70	0.86	0.51	0.40	0.09	–	–	–	–	0.35	0.65
14	70	0.86	0.48	0.42	0.10	–	–	–	0.13	0.37	0.50
15	70	0.86	0.48	0.41	0.11	–	–	–	–	0.50	0.50
16	70	0.86	0.47	0.43	0.10	–	–	–	–	0.39	0.61
17	70	0.86	0.50	0.41	0.09	–	–	–	0.12	0.40	0.48
18	70	0.86	0.48	0.42	0.10	–	–	–	–	0.53	0.47
19	–	0.86	0.55	0.36	0.09	0.01	$4 \cdot 10^{-4}$	$3 \cdot 10^{-3}$	0.05	0.31	0.64
20	70	0.89	0.60	0.35	0.05	–	–	–	–	0.47	0.53
21	70	0.89	0.59	0.34	0.07	–	–	–	–	0.37	0.63
22	70	0.89	0.57	0.37	0.06	–	–	–	0.11	0.33	0.56
23	70	0.89	0.59	0.35	0.06	–	–	–	–	0.39	0.61
24	70	0.89	0.58	0.36	0.06	–	–	–	–	0.39	0.61
25	70	0.89	0.56	0.37	0.07	–	–	–	0.09	0.34	0.57
26	70	0.89	0.58	0.34	0.08	–	–	–	–	0.40	0.60
27	–	0.89	0.63	0.31	0.06	0.005	$1 \cdot 10^{-4}$	$1 \cdot 10^{-3}$	0.03	0.26	0.70

on rearrangement process is similar to that of organosiloxane catalytic polymerization process [36].

2.5. Study of Equilibrium Reactions at Organosiloxane Interaction with Hydrogen Chloride

Hydrolysis reactions of various organochlorosilanes constantly attract attention of researches, as they are the basic means for various organosiloxane production. Hydrogen chloride gas or hydrochloric acid which can significantly effect reaction direction are formed as a rule at organochlorosilane hydrolysis. Thus, it was shown in [38] that in the presence of 29 and 34% hydrochloric acid 1,1,1,3,3,5,5,7,7,7 - decamethyl-tetrasiloxane undergoes catalytic rearrangement with the formation of hexamethyldisiloxane, octamethylcyclotetrasiloxane and linear siloxane with various molecular mass due to siloxane bond cleavage. The higher is hydrochloric acid concentration the deeper are conversions.

Study of trimethylchlorosilane cohydrolysis with organochlorosilanes of various functionality showed that cohydrolysis product compositions depend on siloxane backbone catalytic rearrangement under hydrochloric acid effect [8,9]. According to [39] organochlorosilane hydrolysis is reversible. Values of equilibrium constant of R_3SiCl hydrolysis reaction taking place by equation (5.1) are the same in the studied range of hydrochloric acid concentrations (from 26 to 42% and can be calculated by formula (5.2)

$$R_3SiCl + H_2O \Leftarrow = = = \Rightarrow R_3SiOSi\,R_3 + 2HCl \tag{5.1}$$

$$K_1 = [B(A + B)a]/(Aa) \tag{5.2}$$

where A – R_3SiCl concentration and B – $R_3SiOSiR_3$, a_1 – activity of H_2O, a_2 – activity of HCl. However, taking into consideration the values of a_1 and a_2, given in [39] and [40], we have found that K_1 values increased several times when hydrochloric acid concentration changed from 26 to 42%. Along with hydrochloric acid HCl_{gas} also efficiently cleaves siloxane bond when it is bubbled through organosiloxane. There is a number of patents [41-43] where problems of organochlorosilane cleavage by HCl_{gas} are highlighted. Results given in these works do not allow to identify general regularities of HCl interaction with siloxanes.

The effect of HCl, dissolved in water or water salt solutions as well as in gaseous condition on monofunctional organochlorosilane hydrolysis reversibility is investigated in this paper. The composition study of Me_3SiCl and HMe_2SiCl water hydrolysis products demonstrated close relationship between hydrolysis products and final concentration of formed hydrochloric acid when hydrochloric acid concentration was 25% initial organochlorosilanes were found in reaction products along with $Me_3SiOSiMe_3$ and $HMe_2SiOSiMe_2H$. Their content increases as hydrochloric acid concentration grows. Maximal content of Me_3SiCl and HMe_2SiCl in hydrolysis products achieved 84% from the primary amount at 20 °C and hydrochloric acid concentration – 42.4 and 42.6% respectively. According to the reversible character of the process, and when contact time is long enough, $Me_3SiOSiMe_3$ and HMe_2SiOMe_2H interact with hydrochloric acid with the formation of balanced amounts of related organochlorosilanes and water in $R_3SiCl—R_3SiOSiR_3—HCl—H_2O$ system. R_3SiCl content is determined by hydrochloric acid final concentration. On $Me_3SiOSiMe_3$ and $HMe_2SiOSiMe_2H$ interaction with HCl gas the degree of cleavage results from the balanced character of the process and is related to maximal concentration of hydrochloric acid, produced in the reaction. Thus, maximal cleavage of $Me_3SiOSiMe_3$ and $HMe_2SiOSiMe_2H$ achieved at HCl_{gas} bubbling at the pressure of 1 atm and 20 °C was 84%. 42.4% hydrochloric acid concentration for HMe_2SiCl and 42.6% for Me_3SiCl correspond to this cleavage degree. Hydrogen chloride concentration in organic and water phases and consequently $Me_3SiOSiMe_3$ cleavage depth can be increased due to temperature drop. Maximal cleavage degree of $Me_3SiOSiMe_3$ and $HMe_2SiOSiMe_2H$ (99%) was achieved at the temperature of – 14 °C, when formed water phase was hydrochloric acid of 50% concentration. This explains the choice of temperature ranges for $Me_3SiOSiMe_3$ cleavage from +10 to –15 °C in [45–47]. The increase of $R_3SiOSiR_3$ cleavage degree can be also achieved without temperature drop due to HCl pressure increase resulting in the growth of its concentration in organic acid aqueous phases.

It was found that in the presence of hydrochloric acid solution $Me_2SiOSiMe_3$ cleavage by HCl_{gas} is much faster than in its absence. This allows to suppose that $Me_3SiOSiMe_3$ cleavage takes place not only in organic phase and in aqueous one or in the interface, in the latter cases the reaction is faster thereby. Comparison of $Me_3SiOSiMe_3$ and $HMe_2SiOSiMe_2H$,$(ClCH_2)Me_2SiOSiMe_2(CH_2Cl)$ and $Et_3SiOSiEt_3$ with 40.6% hydrochloric acid taken in such ratio that final concentration of hydrochloric acid is 40% demonstrated that balanced content of $R_3SiOSi\,R_3$ and R_3SiCl depended on substituent type at silicon. Product compositions at $R_3SiOSiR_3$ cleavage by hydrochloric acid (in terms of taken $R_3SiOSiR_3$) is given below

$$\underset{63.7\%}{HMe_2SiOSiMe_2H} \underset{H_2O}{\overset{2HCl}{\Longleftarrow = = = = \Longrightarrow}} \underset{36.3\%}{2HMe_2SiCl} \tag{5.3}$$

$$\underset{62.1\%}{Me_3SiOSiMe_3} \underset{H_2O}{\overset{2HCl}{\Longleftarrow = = = = \Longrightarrow}} \underset{37.9\%}{2Me_3SiCl} \tag{5.4}$$

$$\underset{86.7\%}{(ClCH_2)Me_2SiOSiMe_2(CH_2Cl)} \underset{H_2O}{\overset{2HCl}{\Longleftarrow = = = = \Longrightarrow}} \underset{13.3\%}{2(ClCH_2)Me_2SiCl} \tag{5.5}$$

$$\underset{90.2\%}{Et_3SiOSiEt_3} \underset{H_2O}{\overset{2HCl}{\Longleftarrow = = = = \Longrightarrow}} \underset{9.8\%}{Et_3SiCl} \tag{5.6}$$

Balanced content of $R_3SiOSiR_3$ increases with the growth of the size of substituents at silicon in the following sequence

$$(Et_3Si)_2O > [Me_2(ClCH_2)Si]_2O > (Me_3SiO)_2 \cong (HMe_2Si)O_2$$

This also occurs on Me_3SiCl, HMe_2SiCl, Et_3SiCl and $(ClCH_2)Me_2SiCl$ hydrolysis with water at such reagent ratios that hydrochloric acid final concentration is 40%, which points to the balanced character of reaction mixture compositon both under organosiloxane cleavage by hydrochloric acid and R_3SiCl hydrolysis.

The decrease of organochlorosilane balanced content with the growth of the size of substituents at silicon was also observed at $R_3SiOSiR_3$ cleavage by HCl_{gas}. Thus, on interaction with HCl_{gas} at − 10 °C conversion for $Me_3SiOSiMe_3$ and $HMe_2SiOSiMe_2H$ was 98%, for $(ClCH_2)Me_2SiOSiMe_2(CH_2Cl)$ − 20% and for $Et_3SiOSiEt_3$ − 14% in similar sequence organodisiloxane cleavage rate decreases. $R_3SiOSiR_3$

balanced content increase may result from the growth of intermediate R_3SiOH stability and their content in an organic phase as the size of substituents at silicon increases. R_3SiOH effect on the process can be shown as follows

$$\begin{aligned} R_3SiOSiR_3 + 2HCl &\Leftarrow\!=\!\Rightarrow R_3SiOH \cdot HCl \\ &+ R_3SiCl \Leftarrow\!=\!\Rightarrow 2R_3SiCl + H_2O \end{aligned} \tag{5.7}$$

Dependence of product composition on R_3SiCl hydrolysis and hydrochloric acid interaction with $R_3SiOSiR_3$ on final concentration of the produced hydrochloric acid is the result of hydrogen chloride activity change when bonded by water with formation of hydrate complexes. The lower is hydrochloric acid concentration the lower is HCl reactivity, as with hydration degree growth energy consumtion for complex destruction increases. R_3SiCl absence (in the range of used analytic method sensitivities) in hydrolysis products at hydrochloric acid low concentrations (below 25%) shows that at molar ratio of H_2O to HCl equal to 6 or higher the process is actually irreversible. Molar ratio of H_2O to HCl equal to 6 corresponds to $HCl^+ \cdot 6H_2O$ complex and maximal saturation of the first hydrate layer for oxonium complex $[H_3O^+5H_2O]Cl$. When hydrochloric acid concentration is more than 25% hydration degree is below maximal, which results in HCl reactivity increase in regard of siloxane bond. Thus, saturated solution of hydrochloric acid with 36.6% concentration (at 20 °C and atmospheric pressure) corresponding to average composition of hydrate complex $HCl \cdot 3, 5H_2O$ demonstrated high activity to $Me_3SiOSiMe_3$ and $HMe_2SiOSiMe_2H$. Unlike HCl water reactivity drops with the increase of hydrochloric acid concentration as energy consumption necessary for destruction of hydrate complexes with HCl increases. Hydration influence on hydrolysis is clear from various heat effects on Me_3SiCl hydrolysis with great excess of water and concentrated hydrochloric acid. At Me_3SiCl hydrolysis with hydrochloric acid in conditons providing HCl_{gas} formation the process is endothermal (reaction mixture temperature decreases). This results from low heat effect of hydrolytic reaction with HCl_{gas} production ($\Delta H(1) - 2.8$ kcal/mol); calculated on the base of Me_3SiCl, $Me_3SiOSiMe_3$, H_2O, HCl_{gas} formation heats, given in [47], and it does not compensate energy spent on HCl hydrate complex destruction.

Me_3SiCl hydrolysis by large excess of water is accompanied by significant heating of the reaction mixture, as high energy of HCl hydration (−75, 2kJ/mol) provides exothermal effect. $Me_3SiCl—H_2O—HCl—Me_3SiOSiMe_3$ system balanced composition dependence on solvation process at HCl and H_2O interaction is evident from reaction (5.1) thermodynamics with regard of reagent conditions

$$2Me_3SiCl_{aq} + H_2O_{aq} \Leftarrow = \Rightarrow Me_3SiOSiMe_{3_{aq}} + 2\,HCl_{aq} \qquad (5.8)$$

where the following record can be made

$$\Delta G_{(298K)} = \Delta H_{(298K)} - 293.15\Delta S_{(298K)} \qquad (5.9)$$

Here

$$\begin{aligned}\Delta H = {} & \Delta f H(Me_3SiOSiMe_{3_{aq}}) - 2\Delta f H(Me_3SiCl_{aq}) \\ & - \Delta f H(H_2O_{aq}) + 2\Delta f H(HCl_{aq}) \qquad (5.10)\end{aligned}$$

Enthalpy of HC_{aq} formation depends on a number of water moles accounted for HCl mole in aqueous solution. According to [45] this dependence can be expressed by a formula

$$\Delta f H(HCl_{aq})\Delta G = -126.6 - 9.3366M + 6.84218M^2 \qquad (5.11)$$

Other formation enthalpies were taken from [44]. Then

$$\Delta H = 239.1 + 2\Delta f H(HCl_{aq})\Delta G \qquad (5.12)$$

ΔS value is determined by reaction (5.9) component entropies; HCl_{aq} entropy can be found from HCl vapor pressure above hydrochloric acid acqueous solution, taken from [46], enthalpies of HCl vapor from HCl acqueous solution, calculated by equation (5.11) and absolute entropy of HCl_{gas} equal to 186.8 J/(mol. K) [47]. Other component entropies were taken from [48]. Then

$$\Delta S = -186.4 + 2S(HCl_{aq})J/K \qquad (5.13)$$

Combining equations (5.9, 5.12, 5.13) we will have

$$\Delta G = -RT\ln K = 294 + (2\Delta fH(HCl_{aq}) - 0.29315S(HCl_{aq})kJ \qquad (5.14)$$

Notice: a) Pressure of HCl vapor over hydrochloric acid with concentration of 40.6 and 42.6% was calculated by the equation Ln p(HCl) mm Hg $= -19.851 + 9.7425\,(c/10) - 0.8375\,(c/10)^2$, found for concentration range of 38–42%; b) Calculated; c) Experimentally found.

"K" value can be calculated by experimental data regarding organic and aqueous phase compositions (see Tab. 5.1)

$$K = n_1(Me_3SiOSiMe_3)(n_2(HCl))^2/n_3(H_2O)(n_4(Me_3SiCl))^2 \qquad (5.15)$$

Here n_1 $(Me_3SiOSiMe_3)$, $n_2(HCl)$, $n_3(H_2O)$, $n_4(Me_3SiCl)$ – number of moles of each component.

RTlnK value was converted to the total number of moles equal to 6, conventional value, chosen in regard of reaction (5.10) stoichiometry Experimental data are described by equation (5.16).

$$\begin{aligned} -RT\ln K &= 299.7 \pm 7. + (1.987 \pm 0.05)5.\Delta f H(HCl_{aq}) \\ &\quad - 0.29315S(HCl_{aq})kJ, \ r = 0.998 \end{aligned} \qquad (5.16)$$

Agreement of theoretical and found by the least squares method coefficients of equations (5.14) and (5.16) testifies to the actual equilibrium between aqueous and organic phases. Equation (5.15) advantage against equation (5.2) is its better suitability for calculations. Morevoer on the ground of equation (5.16), we can determine reaction (5.8) enthalpy from equilibrium data at the same temperature due to the relationship between $\Delta f H(HCl_{eq})$ and hydrochloric acid concentration. This possibility was not noticed by the authors of [39] who had determined reaction (5.8) enthalpy by measuring balanced composition dependence on temperature.

R_3SiCl hydrolytic reaction and $R_3SiOSiR_3$ cleavage by hydrogen chloride are possible in any of available phases(gas, organic, aqueous) as well as on their interface as each component is in the equilibrium with

TABLE 5.1 Balanced Compositions and Aqueous Phase Properties in $Me_3SiCl - H_2O - HCl - Me_3SiOMe_3$ system

Balanced Compositions (experimental)					*Index*			
HCl mol, (%)	*H_2O moles*	*$(Me_3Si)_2O$ mol*	*Me_3SiCl moles*	*ΔG^b kJ*	*ΔG^c kJ(in terms of 6 moles)*	*ΔfH (HCl_{aq})*	*$p(HCl)^a$ mm. Hg.*	*$S(HCl_{aq})$ J mol. K*
0.686 (25)	4.162	0.343	0.0026	−21.1	−24.4	−157.7	1.5	19.2
0.823 (30)	3.885	0.412	0.019	−12.9	−15.1	−155.2	10.6	11.5
0.933 (34)	3.663	0.467	0.0775	−7.11	−8.28	−152.5	50.5	7.3
0.987 (36)	3.552	0.494	0.163	−3.97	−4.60	−151.2	105	5.8
1.042 (38)	3.441	0.521	0.402	−0.04	−0.04	−149.8	210	4.6
1.097 (40)	3.330	0.549	0.595	1.41	1.52	−148.6	399	3.5
1.114 (40.6)	3.296	0.557	0.832	2.91	3.01	−148.2	475^a	3.4
1.152 (42)	3.219	0.576	2.451	7.87	6.38	−147.2	709	3.1
1.168 (42.6)	3.185	0.584	4.583	10.8	6.80	−146.9	832^a	3.0

each phase. The possiblity of all components of the reaction system presence in each phase is confirmed by GLC method. When the reaction system composition was studied on Me_3SiCl hydrolysis with water and dioxane mixture with toluene, providing homogenity (Me_3SiCl – 2.5%, H_2O – 0.8%, dioxane – 91.2%, toluene – 5.5 wt%) simultaneous presence of significant amounts of $R_3SiOSiMe_3$, Me_3SiCl, Me_3SiOH and HCl was shown.

Hydrochloric acid analysis formed on Me_3SiCl hydrolysis demonstrated the presence of organosilicon product. Its total content was 0.007 mol/l in terms of Me_3SiCl (determined with atomic adsorption spectroscopy by silicon content). Relationship between HCl and water activity under hydrolysis and hydration processes is still more evident under hydrolysis by salt solutions. On Me_3SiCl hydrolysis by NaCl, KCl, NH_4Cl, $CaCl_2$, LiCl solutions, HCl effect on hydrolysis products composition depended critically on the strength of hydrate complexes, formed by these salts. On Me_3SiCl hydrolysis by NaCl, KCl, NH_4Cl saturated solutions at hydrochloric acid concentration higher than 25%, Me_3SiCl and $Me_3SiOSiMe_3$ ratio in reaction products is actually the same as under hydrolysis by water. In the presence of $CaCl_2$ and LiCl saturated solutions hydrolysis is inhibited. Thus, if under hydrolysis by water the balanced composition of Me_3SiCl and $Me_3SiOSiMe_3$ is achieved very quickly after the reagents have been mixed, in $CaCl_2$ and LiCl presence period when the equilibrium is achieved increases several times. In organic phase increased content of Me_3SiCl is gradually decreased to equilibrium. Period of system balancing increases several times on $CaCl_2$ solution transfer to LiCl solutions of similar concentrations and with the increase of relative share of organic phase. Increase of period for system balancing at Me_3SiCl hydrolysis by $CaCl_2$ and LiCl solutions results from the activity decrease of water bonded to hydrate complexes with salts.

The other peculiarity of Me_3SiCl hydrolysis in the presence of $CaCl_2$ and LiCl saturated solutions is in the presence of balanced amounts of Me_3SiCl in reaction products already at low HCl concentration in the aqueous phase. Me_3SiCl balanced content achieves 60% on Me_3SiCl hydrolysis by LiCl saturated solution at HCl concentration in aqueous phase – 7%, $CaCl_2$ – 26% and by water – 42%. The equilibrium in Me_3SiCl—$Me_3SiOSiMe_3$ system is shifted towards Me_3SiCl as HCl concentration increases in aqueous-salt phase. With the decrease of salt concentration the preset Me_3SiCl — $Me_3SiOSiMe_3$ composition is achieved at higher HCl concentrations. Comparison of hydrolytic-product composition at similar concentrations of $CaCl_2$ and LiCl solutions demonstrated that in the case of LiCl the equilibrium is shifted towards higher Me_3SiCl content. Thus for 42% $CaCl_2$ and LiCl solutions involving 9% HCl, molar ratio of $[Me_3SiCl]/[Me_3SiOSiMe_3]$ is 0.01 and 8.5 respectively. Large efficiency of HCl effect in aqueous solutions of metal chlorides is the result of solution ion strength increase and decrease of HCl dissociation degree in a solution.

Study of $Me_3SiOSiMe_3$ interaction with HCl gas in the presence of $CaCl_2$ solution showed that $Me_3SiOSiMe_3$ cleavage is faster than in hydrochloric acid presence. An induction period is observed on the initial stage in the same way as the course of $Me_3SiOSiMe_3$ cleavage in salt absence which is evidently due to the necessity of aqueous-salt phase formation, promoting process activation. Water bonding to strong hydrate complexes in $CaCl_2$ presence results in more considerable degree of $Me_3SiOSiMe_3$ cleavage. It agrees with data of [42] proving that at reagent ratios providing that maximum hydration degree of water-formed salts does not exceed 6 molecules of water per 1 molecule of salt, $Me_3SiOSiMe_3$ quatitative cleavage is possible at 20 °C in the presence of water-free $ZnCl_2$, $CaCl_2$ and $MgCl_2$ salts. The salts move the equilibrium towards Me_3SiCl. Investigation results of Me_3SiCl hydrolysis by salt solutions prove that salt effect on the process is determined by hydration energy. HCl slightly decomposes hydrate complexes of the considered salts due to high energy of $CaCl_2$ and LiCl hydration. HCl solubility in $CaCl_2$ and LiCl solutions is lower than in water but low degree of HCl hydration in these salt solutions promotes its high activity in siloxane bond cleavage reaction which agrees with the experiment. HCl concentration in LiCl solutions is lower than in $CaCl_2$ solutions at similar salt concentrations. This is because LiCl molar concentration increase in comparison with $CaCl_2$ and H_2O bonding degree in hydrate complexes is higher. For 42% $CaCl_2$ solution molar ratio of water and salt is 8.5 and for LiCl - 3.2. Taking into account that coordination number for inside hydrate sphere for Ca^{+2} is 6 and for Li^{+1} – 4 [49, 50] at the chosen concentration in LiCl solution water is bonded much stronger than in $CaCl_2$ solution. This results in a larger effect of LiCl on Me_3SiCl hydrolysis than that of $CaCl_2$.

2.6. Study of Catalytic Rearrangement of Organosiloxanes at Interaction with Organochlorosilanes

α, ω-Dichlorooligodimethylsiloxane synthesis is of practical and theoretical interest. Such compounds are widely used to produce organosiloxanes of tailor-made composition and structure [6] and block-copolymers [51]. Study of equilibrium and unequilibrium regularities of α, ω-dichlorooligodimethylsiloxanes also allows to appreciate the peculiarities of Si—O and Si—Cl bond mutual effect on their reactivity. Basic method of said oligomer synthesis can be a reaction of dimethyldichlorosilane (DMDCS) partial hydrolysis or catalytic rearrangement on DMDCS interaction with dimethylcyclosiloxanes [52].

Regularities of octamethylcyclotetrasiloxane (D_4) catalytic telomerization reaction with DMDCS in the presence of electrophilic catalysts such as Lewis acids ($FeCl_3$, $AlCl_3$, $ZnCl_2$), their hydrates ($FeCl_3 \cdot 6H_2O$, $AlCl_3 \cdot 6H_2O$, $Al_2(SO_4)_3 \cdot 18H_2O$, $ZnCl_2 \cdot 4H_2O$), inorganic acids (H_2SO_4, H_3PO_4), aromatic sulfuric acids ($PhSO_3H$, 4-$MeC_6H_4SO_3H$, 3-Me-4-$(NO_2)C_6H_3SO_3H$) and their mixtures with H_3PO_4 were investigated. Catalytic rearrangement reaction on D_4 interaction with DMDCS can be shown in the following equation

$$a[Me_2SiO]_4 + bMe_2SiCl_2 \overset{Cat.}{\Longleftrightarrow} c\,Cl(Me_2SiO]_{4n}SiMe_2Cl + d[Me_2SiO]_m \qquad (6.1)$$

Study of various catalyst relative activities in the process of rearrangement was carried out at molar ratio of $Me_2SiCl_2 : D_4 = 1 : 10$. When Lewis acid hydrates were used DMDCS quantity was taken in excess in regard of water involved in catalysts. Study of anhydrous $FeCl_3$, $AlCl_3$, $ZnCl_2$ activity demonstrated that reaction rate is very low in their presence. At the same time their hydrates showed high catalytic activity and fast consumption of D_4 and DMDCS is observed. As water in hydrate complexes interacts with DMDCS with hydrogen chloride isolation hydrate complex catalytic activity is determined by the activity of hydrogen chloride complex with Lewis acid. This is also confirmed by high catalytic activity of anhydrous Lewis acid when hydrogen chloride is passed through the reaction mass or on water introduction into reaction system involving anhydrous Lewis acid.

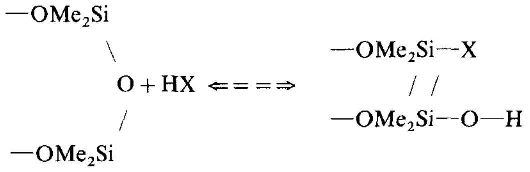
Comparison of activity of catalysts based on Lewis and organic acid in terms of time of D_4 50% conversion at 1% catalyst concentration showed the activity decrease in a series

$$FeCl_3 \cdot 6H_2O > H_3PO_4 > H_2SO_4 > AlCl_3 \cdot 6H_2O > ZnCl_2 \cdot 4H_2O$$

Study of DMDCS and D_4 conversion dependence on time in the presence of 1% series of Lewis acid and inorganic acid hydrate complexes was carried out. The obtained data testifies that there is an induction period on D_4 conversion kinetic curves which is absent on DMDCS conversion curves. It should be mentioned that telomerization in the presence of the studied catalysts allows us to bring the reaction to the equilibrium (> 0.5% DMDCS and 5% D_4). The investigation of catalytic activity of H_2SO_4/H_3PO_4 binary mixture (1% + 1%) proved that its activity exceeded the activity by either component at 2% concentration. However in this case the induction period of the reaction is long because of binary catalyst low solubility in the reaction mixture. In this regard sulfuric acid-based catalysts, soluble in the studied reaction mixture are of significant interest. Benzenesulfuric acid, p-toluenesulfuric acid, 4-methyl-3-nitrobenzenesulfoacid were studied as arylsulfuric acids. In the presence of 1% aromatic sulfoacids the process induction period is long, and their activity is a bit lower than that of phosphoric acid. DMDCS is completely consumed within 1–1.5 hours and the equilibrium in D_4 process is achieved within 8–10 hours. When aromatic sulfoacids in mixture with H_3PO_4 are used, the induction period is several times reduced and the reaction rate increases. In terms of D_4 consumption catalytic system activity changes in a series

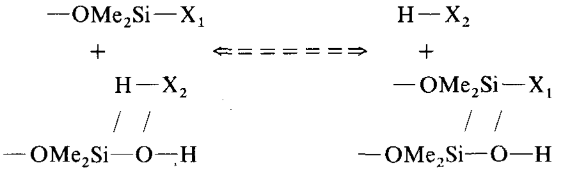
$$3\text{-Me-4-}(NO_2)C_6H_3SO_3H/H_3PO_4 \cdot > PhSO_3H/H_3PO_4 \cdot$$
$$> 4\text{-Me}C_6H_4SO_3H/H_3PO_4 > H_2SO_4/H_3PO_4.$$

The induction period for these systems reduces in the same sequence. High activity of acid mixture can be explained by multistage telomerization. The possible pathway of telomerization process can be demonstrated as a series of consecutive-parallel reactions

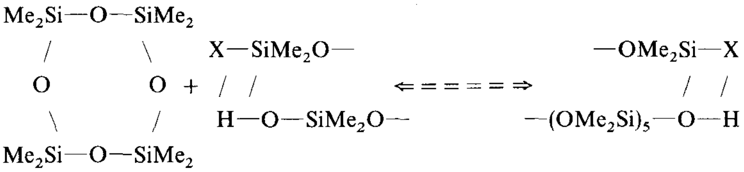


$$\begin{array}{l} —OMe_2Si \\ \quad\quad \backslash \\ \quad\quad O + HX \Leftarrow\!=\!=\!\Rightarrow \\ \quad\quad / \\ —OMe_2Si \end{array} \quad \begin{array}{l} —OMe_2Si—X \\ \quad / \; / \\ —OMe_2Si—O—H \end{array} \qquad (6.2)$$

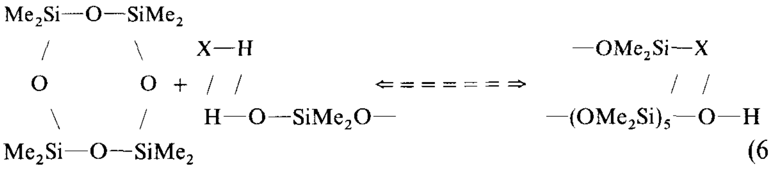
$HX = HX_1$ or HX_2 – acid catalysts used



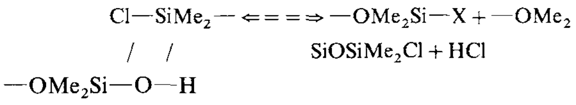
$$\begin{array}{c} —OMe_2Si—X_1 \\ + \\ H—X_2 \\ / \; / \\ —OMe_2Si—O—H \end{array} \Leftarrow\!=\!=\!=\!=\!=\!=\!\Rightarrow \begin{array}{c} H—X_2 \\ + \\ —OMe_2Si—X_1 \\ / \; / \\ —OMe_2Si—O—H \end{array} \qquad (6.3)$$



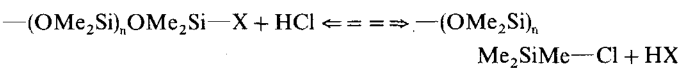
$$\begin{array}{ccc} & Me_2Si—O—SiMe_2 & \\ / & & \backslash \\ O & & O \\ \backslash & & / \\ & Me_2Si—O—SiMe_2 & \end{array} + \begin{array}{l} X—SiMe_2O— \\ \; / \; / \\ H—O—SiMe_2O— \end{array} \Leftarrow\!=\!=\!=\!=\!=\!\Rightarrow \begin{array}{r} —OMe_2Si—X \\ / \; / \\ —(OMe_2Si)_5—O—H \end{array} \qquad (6.4)$$



$$\begin{array}{ccc} & Me_2Si—O—SiMe_2 & \\ / & & \backslash \\ O & & O \\ \backslash & & / \\ & Me_2Si—O—SiMe_2 & \end{array} + \begin{array}{l} X—H \\ \; / \; / \\ H—O—SiMe_2O— \end{array} \Leftarrow\!=\!=\!=\!=\!=\!=\!\Rightarrow \begin{array}{r} —OMe_2Si—X \\ / \; / \\ —(OMe_2Si)_5—O—H \end{array} \qquad (6.5)$$



$$\begin{array}{l} \quad Cl—SiMe_2— \\ \quad\; / \; / \\ —OMe_2Si—O—H \end{array} \Leftarrow\!=\!=\!=\!\Rightarrow \begin{array}{l} —OMe_2Si—X + —OMe_2 \\ \quad SiOSiMe_2Cl + HCl \end{array} \qquad (6.6)$$



$$—(OMe_2Si)_nOMe_2Si—X + HCl \Leftarrow\!=\!=\!=\!\Rightarrow \begin{array}{l} —(OMe_2Si)_n \\ Me_2SiMe—Cl + HX \end{array} \qquad (6.7)$$

There are differences in activity on the stage of the reaction centre formation (equation 6.2) and its reactions by siloxane bond (equations 6.4

and 6.5) for each catalyst. However the exchange reaction (equation 6.3) may result in total increase of reaction rate as the rates of reaction centre formation and its interaction with siloxane bond can increase. Rate constant of DMDCS and D_4 consumption were calculated in terms of reversible reactions of the first order. Constant values are given in Table 6.1. For mixed catalysts based on aromatic sulfo- and phosphoric acids each reagent consumption rate on kinetic sites of the curves does not depend on current concentration of other reagent and the reaction is the first order one for each reagent. This leads to the conclusion that in the course of telomerization each reagent enters into a number of independent reactions determining the observed kinetic peculiarities, and observed order of the reaction is imagined and constant values are conditional. Reactions with DMDCS, with end dimethylchlorosilane group in linear chain and with the growing polymer siloxane chain are possible for D_4. Higher rate constants of DMDCS consumption in comparison with D_4 show that along with dimethylsiloxane cycle opening (equation 6.8) DMDCS simultaneously reacts by siloxane chain with formed α,ω-dichlorooligodimethylsiloxane (equation 6.9)

$$[Me_2SiO]_4 + Me_2SiCl_2 \overset{Cat.}{\Longleftarrow\!=\!=\!\Longrightarrow} Cl(Me_2SiO]_5SiMe_2Cl \qquad (6.8)$$

$$Me_2SiCl_2 + Cl(Me_2SiO]_5Me_2SiCl \overset{Cat.}{\Longleftarrow\!=\!=\!\Longrightarrow} Cl(Me_2SiO]_n$$
$$Me_2SiCl + Cl(Me_2SiO]_{5\text{-}n}Me_2SiCl \qquad (6.9)$$

In order to find out the reaction rate effect on catalyst component concentration D_4 telomerization with DMDCS by 3-Me-4-(NO_2)

TABLE 6.1 Values of DMDCS and D_4 consumption rate constants in the reactions catalyzed by complex catalysts based on aromatic sulfoacids and H_3PO_4

Catalyses $ArSO_3H/H_3PO_4$ *(0, 1mol/l:0,046 mol/l)*	k_{DMDCS}, s^{-1}	k_D, s_{-1}
$PhSO_3H/H_3PO_4$	$(0.60 + 0.038)\cdot 10^{\ 2}$	$(1.84 + 0.05)\cdot 10^{-3}$
$4\text{-}MeC_6H_4SO_3H/H_3PO_4$	$(1.67 + 0.017)\cdot 10^{-2}$	$(1.77 + 0.05)\cdot 10^{-3}$
$3\text{-}Me\text{-}4\text{-}(NO_2)C_6H_3SO_3H/H_3PO_4$	$(3.14 + 0.060)\cdot 10^{-3}$	$(2.72 + 0.04)\cdot 10^{-3}$

$C_6H_3SO_3H/H_3PO_4$ catalytic mixture was carried out at various catalyst component ratios. Analysis of relationship between rate constant K_D values and catalyst component concentration showed that total reaction order in terms of catalysts was 3, order in terms of H_3PO_4 was 1 in terms of 3-Me-4-$(NO_2)C_6H_3SO_3H$-2.

Thus, the equation of D_4 consumption rate looks as follows

$$W_D = K_D[D_4][H_3PO_4][3\text{-Me-}4\text{-}(NO_2)C_6H_3SO_3H]^2 \qquad (6.10)$$

Study of DMDCS:D_4 initial ratio effect on telomerization reaction rate was carried out. Reaction pathway at initial ratios of DMDCS: D_4 = 1:10, 1:2 and 1:1 with H_3PO_4(0.25 mol/l), and 3-Me-4-$(NO_2)C_6H_3SO_3H$(0.012 mol/l) mixture grows as DMDCS content increases. Values of D_4 rate constant consumption are shown in the Table 6.2.

At 10 times change of DMDCS:D_4 ratio the value of rate constant k_D increases more then 16 times.

3. CONCLUSION

In the result of the investigations we can formulate a number of general regularities for reactions studied.

1. For rearrangement reactions with Si—O—Si or Si—O—Si and Si—OR bond participation equilibrium constant does not depend on temperature, which indicates that reaction enthalpy is close to zero.
2. The studied reactions are well described by kinetic equations for reversible reactions with the identical constant values up to a high level of conversion.

TABLE 6.2 Values of D_4 consumption constant at various concentrations and component ratios of the catalytic mixture. 3-Me-4-$(NO_2)C_6H_3SO_3H/H_3PO_4$

H_3PO_4 mol/l	*3-Me-4-$(NO_2)C_6H_3SO_3H$ mol/l*	*Constant of D_4 consumption rate, s^{-1}*
0.17	0.023	$106 \cdot 10^{-5}$
0.10	0.046	$272 \cdot 10^{-5}$
0.05	0.023	$35.5 \cdot 10^{-5}$
0.025	0.012	$4.4 \cdot 10^{-5}$
0.10	0.023	$66 \cdot 10^{-5}$

3. The initial concentration effect of all magents on reaction rate constants was observed for all studied reactions. This effect is determined by the formation of several types of reaction centres with various reactivity catalysts.

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