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Polycondensation and disproportionation of an oligosiloxanol in the presence of a superbase

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Abstract

Kinetics of reactions of model oligosiloxanols, 1,1,3,3,3-pentamethyldisiloxane-1-ol (MDH) and 1,1,3,3,5,5,5-heptamethyltrisiloxane-1-ol (MD$_2$H), which occur in the presence of phosphazenium superbase, hexapyrrolidine-diphosphazenium hydroxide, in an acid–base inert solvent, toluene, was studied using sampling and gas chromatographic analysis method. In addition, kinetics of reactions of MDH and MD$_2$H with trimethylsilanol (MH) was studied. In the MDH and MD$_2$H systems the oligosiloxanol condensation competes with the oligosiloxanol disproportionation, the latter being the dominating process. The disproportionation products, i.e. MD$_{n+1}$H and MD$_{n-1}$H, $n = 1, 2, \ldots$ undergo analogous consecutive disproportionation and condensation reactions. The kinetic law was derived and rate parameters determined from initial rates and by computer simulation to the best agreement with experimental data. Both competing reactions, the disproportionation and the condensation, conform to the same general kinetic law being first internal order in substrate and first order in catalyst. Activation parameters of these reactions were determined. The results were interpreted in terms of a bimolecular mechanism in which nucleophilic attack of the silanolate anion directed to silicon of the silanol group causes the cleavage of one of its geminal bonds to oxygen, either the one to hydroxyl leading to condensation or the one to siloxane which leads to disproportionation. The latter is faster as the silanolate is a better leaving group compared with OH$^-$. Moreover, in the pentacoordinate silicon transition state (or intermediate) the siloxane substituent preferentially enters the apical position, thus driving the OH substituent into the unreactive equatorial position. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

There has been considerable interest in the study of processes involving silanol condensation as they are commonly used in the synthesis of siloxane polymers, for review see [1–4]. Strong bases such as alkali hydroxides or silanolates and ammonium hydroxide or silanolates, are known to be very efficient catalysts for these processes [5–8]. For a long time it had been accepted that the homofunctional condensation of silanol end groups was the sole reaction in the polycondensation system. Monomeric silanol substrates were exploited in kinetic studies and functional group conversion or monomer conversion was followed. Thus, reactions of the siloxane bond cleavage could have escaped the notice of researchers. However, studies performed in the 80 s, in which some oligomer substrates were explored as models, revealed that the polycondensation carried out in the presence of strong bases is greatly dominated by dismutation (disproportionation) processes [9–12]. These processes involve siloxane cleavage and lead to randomisation of oligomers and polymers by exchange of terminal siloxane units. The dismutation of oligosiloxanol was so fast compared with the condensation that kinetic studies of this dismutation were performed neglecting the silanol condensation [10,11].

Finding a model system to study the kinetics of silanol–silanol condensation and siloxane bond cleavage pro-

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cesses using basic catalysts is difficult. It has been demonstrated that counter-cations play a considerable role in the disproportionation, which proceeds particularly fast in the presence of cations, which strongly interact with the silanolate anion [10], such as Li^+. Thus, a system where the interaction was weak seemed to be more plausible for the study of the silanol–silanol condensation reaction. Most studies have been performed using alkali metal bases in acid–base reactive solvents, which dissolve the base well, such as dioxane–water [11,12], methanol [13,15], deuterated water [14] and isopropanol [9]. These solvents are also known to be active in the Si–O bond cleavage leading to a very complex reaction system. This is also the reason for which they are not used in industrial synthesis of linear polysiloxanes. Thus, a non-polar acid–base inert solvent would be preferable in this study. However, the solubility of strong bases in these solvents is limited. Moreover, intensive ion association, in particular, the formation of strong aggregates of silanolate intermediates [15,16], and the association of silanolate with silanol and water [17] occurs. These association phenomena additionally complicate the kinetics of the polycondensation leading to fractional apparent order in catalyst [18].

Some years ago very strong bases, peraminooligophosphazenium hydroxides, were synthesised [19,20]. Some of them are soluble in aromatic hydrocarbon, such as toluene, and proved to be very efficient catalysts of siloxane polymerisation and silanol polycondensation [21]. This makes it possible to investigate the polycondensation in a neutral solvent system close to that used in industrial manufacturing of polydimethylsiloxanes. These bases have bulky phosphazenium cations in which the charge is strongly delocalised. The cations should interact only very weakly with negatively charged base, such as the silanolate ion, and the association phenomena with other nucleophilic species in the system should be of minor importance. Studies of the kinetics of silanol condensation and siloxane disproportionation in the presence of these catalysts are of particular interest. Using a suitable model of oligosiloxanol substrates the rates of the silanol condensation could be directly compared with processes involving siloxane cleavage, such as the disproportionation, in the same base–siloxanol system. For this purpose it was necessary to use analytical methods permitting the measurement of various oligosiloxane and oligosiloxanol concentrations formed in the reaction system. Gas chromatography is particularly useful in this respect.
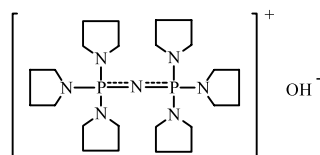
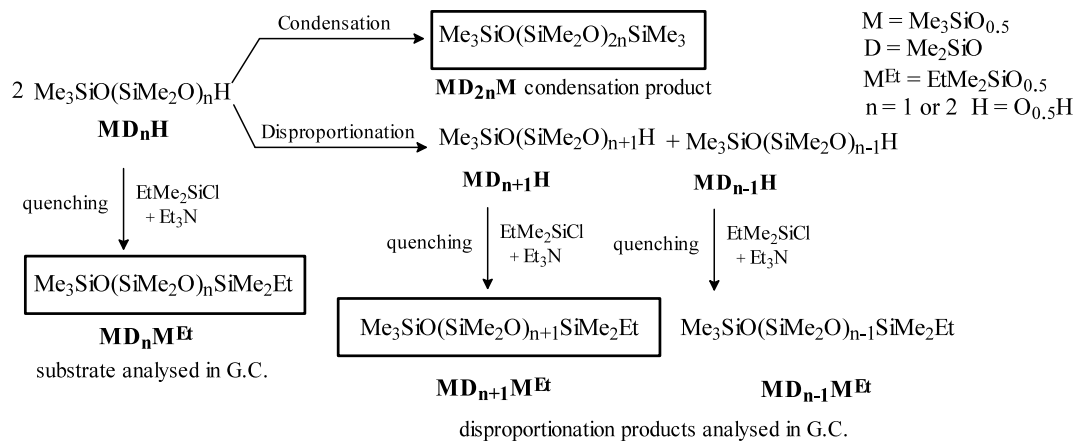Scheme 1.

2. Results and discussions

2.1. The description of model systems

The model substrates used for the kinetic studies were 1,1,3,3,3-pentamethyl-1,3-disiloxane-1-ol, (MDH), and 1,1,3,3,5,5,5-heptamethyl-1,3,5-trisiloxane-1-ol, (MD₂H), while 1,1,1,3,3,3-hexapyrrolidinyl-1,3-diphosphazenium hydroxide, Scheme 1, was used as the catalyst. Bulky pyrrolidinyl substituents at phosphorus should reduce the ability of the phosphazenium cation to associate with nucleophilic species. The reaction was performed in a toluene solution and was followed by sampling and gas chromatographic analysis. The reaction was quenched by addition of ethyldimethylchlorosilane in a mixture with triethylamine in THF solution. Thus, the expected products of the primary reactions analysed by gas chromatography are formed according to Scheme 2, $n = 1$ and 2 for substrates MDH and MD₂H, respectively. Commonly used quenching agent $Me_3SiCl + Et_3N$ would convert MD_nH to MD_nM, thus would not permit the differentiation between condensation and disproportionation products.

Me_3SiOH was used as the substrate to study the pure silanol condensation reaction in the absence of any dismutation processes. The mixed systems MH + MDH and MH + MD₂H were also explored.

The condensation reactions lead to generation of water, which may form a separate phase. However, the phase separation only occurs in the polysiloxanol systems at a late stage of the reaction studied when most of the reactant was consumed. Thus, it was assumed that the whole reaction proceeds in a one-phase system. Since the amount of water produced in the reactions of MDH and MD₂H is low, it is also assumed that the rates of these reactions are not significantly affected by water. However, the effect of water is considerable in the case of the trimethylsilanol (MH) solution system, where condensation is the exclusive process. Moreover, MH is a considerably weaker acid than MD_nH [22], thus more comparable to water. The reaction slows down as it proceeds and is strongly suppressed when the solution becomes hazy indicating phase separation (Fig. 1). Evidently most of the catalyst passes to the water phase.

Siloxane hydrolysis, which is reverse to the MD_nH condensation, is not considered as the condensation eventually leading to almost full conversion of MD_nH species. Primary products of disproportionation and condensation are almost the only products in the initial stages of the reaction. Only one secondary product, MDM, appears early in the MDH reaction system reflecting fast condensation of MDH + MH. The balance equations for D units in the substrate and in primary products, Eq. 1 for the reaction of MDH and Eq. 2 for the reaction of MD₂H, was kept fairly well up

$$M = Me_3SiO_{0.5}$$
$$D = Me_2SiO$$
$$M^{Et} = EtMe_2SiO_{0.5}$$
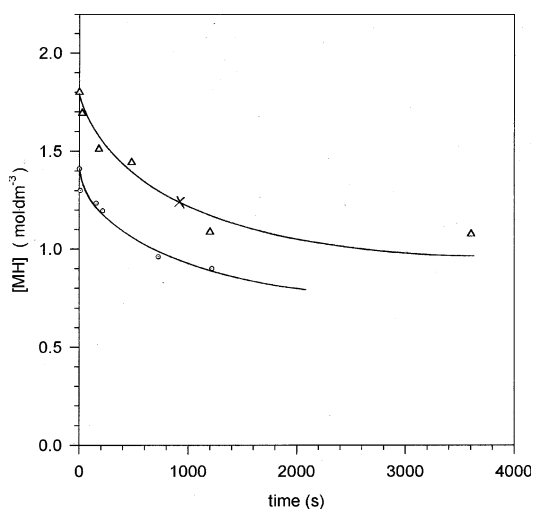$$n = 1 \text{ or } 2 \quad H = O_{0.5}H$$

Scheme 2.

Fig. 1. Substrate conversion-time dependence for the condensation of trimethylsilanol catalysed by 1,1,1,3,3,3-hexapyrrolidinediphosphazenium hydroxide in toluene at 25 °C, ($\triangle$) $[MH]_0 = 1.80$ mol dm^{-3}, ($\bigcirc$) $[MH]_0 = 1.41$ mol·dm^{-3}, $[cat]_0 = 3.60 \cdot 10^{-3}$ mol dm^{-3}, x-marks the moment when the water phase appears.
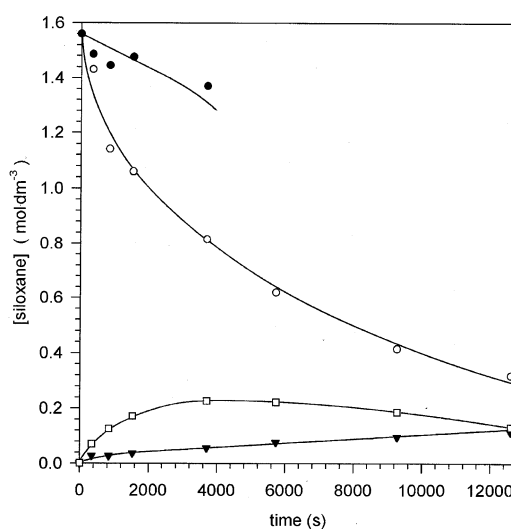

Fig. 2. Substrate conversion-time and product formation-time dependencies for the disproportionation and condensation reactions of 1,1,3,3,3,-pentamethyldisiloxane-1-ol (MDH) catalysed by 1,1,1,3,3,3-hexapyrrolidinediphosphazenium hydroxide in toluene at 25 °C, $[MDH]_0 = 1.56$ mol·dm^{-3}, $[cat]_0 = 9.60 \cdot 10^{-3}$ mol dm^{-3}. ($\bigcirc$) MDH, ($\square$) MD$_2$H, ($\blacktriangledown$) MD$_2$M, ($\bullet$) [MDH]+2[MD$_2$H]+2[MD$_2$M].

to about 30% of the substrate conversion (Figs. 2 and 3). Therefore, in this range secondary processes played a minor role. Thus, the comparison of the initial rate of formation of MD$_2$M and MD$_2$H, the latter is quantitatively transformed to MD$_2$M^{Et} upon quenching, permitted comparison of the rates of condensation and disproportionation of MDH (Fig. 2). Similarly, from the initial rates of formation of MD$_4$M and MD$_3$H transformed to MD$_3$M^{Et}, relative rates for the condensation and disproportionation of MD$_2$H could be deduced (Fig. 3).

$$[MDH] + 2[MD_2M] + 2[MD_2H] \approx [MDH]_0 \qquad (1)$$

$$2[MD_2H] + [MDH] + 3[MD_3H] + 4[MD_4M]$$
$$\approx 2[MD_2H]_0 \qquad (2)$$

The over-all process is more complex because of consecutive reactions of disproportionation and con-

densation of silanols formed according to Scheme 3. Therefore, Eqs. 1 and 2 are approximate. The general balance equation is as follows:

$$\sum_{i=1} i[MD_iH] + \sum_{i=1} i[MD_iM] = n[MD_nH]_0 \qquad (3)$$
$$n = 1 \text{ or } 2$$

It should be pointed out that, although condensation is slower than disproportionation, both reactions can be followed in the MDH system, which is in contrast to much higher disproportionation to condensation rate ratios observed in the presence of some alkali metal silanolates [10].

Since the processes in model systems are complex, two approaches for the analysis of their kinetics were used. First was a simplified analysis based on initial rates neglecting any consecutive reactions. This analysis
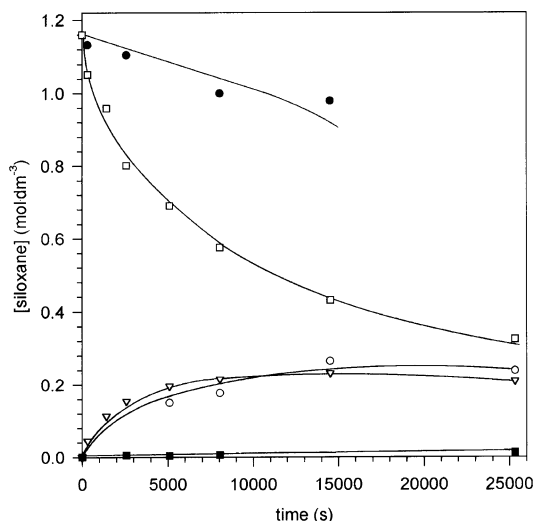
Fig. 3. Substrate conversion-time and product formation-time dependencies for the disproportionation and condensation reactions of 1,1,3,3,3,5,5,5-heptamethyltrisiloxane-1-ol (MD$_2$H), catalysed by 1,1,1,3,3,3-hexapyrrolidinediphosphazenium hydroxide in toluene at 25 °C, [MD$_2$H]$_0$ = 1.16 mol·dm^{-3}, [cat]$_0$ = 3.54·10^{-3} mol dm^{-3}. (□) MD$_2$H, (▽) MD$_3$H, (○) MDH, (■) MD$_4$M, (●) [MD$_2$H]+3/2[MD$_3$H]+1/2[MDH]+2[MD$_4$M].

permitted determination of the kinetic and activation parameters for primary reactions. The other approach was a computer simulation of the kinetic curves to the best agreement with experimental points. This analysis permitted the interpretation of kinetic dependencies at higher substrate conversions and the verification of the assumptions used in the analysis of the initial rate kinetics.

2.2. Initial rate kinetics in MDH and MD$_2$H systems

Results shown in Figs. 2 and 3 indicate that disproportionation and condensation compete with each other and both can be followed separately as they lead to different products. Since the relative rates of the formation of the primary condensation and dispropor-
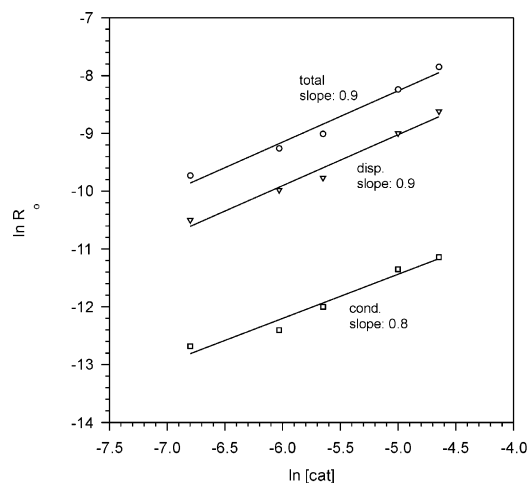

Fig. 4. The dependencies of the initial rates of substrate conversion and product formations on the catalyst concentration for the disproportionation and condensation of MDH catalysed by [(C$_4$H$_8$)$_3$P–N–P(C$_4$H$_8$)$_3$]$^+$ OH$^-$ in toluene at 25 °C, [MDH]$_0$ = 1.52 mol dm^{-3}.
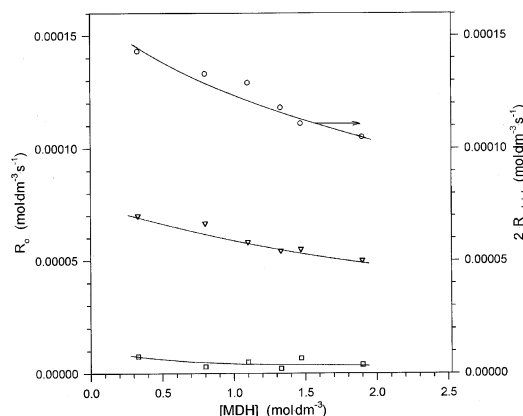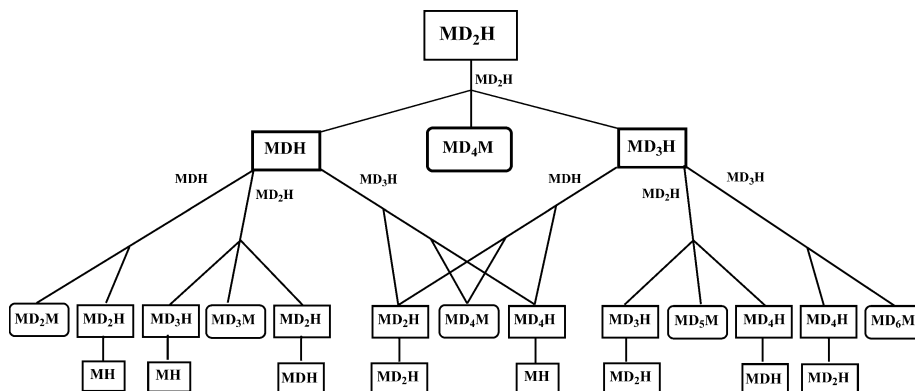

Fig. 5. The dependence of the initial rates of substrate conversion and products formation on initial substrate concentration for the disproportionation and condensation of MDH in toluene at 25 °C catalysed by [(C$_4$H$_8$)$_3$P–N–P(C$_4$H$_8$)$_3$]$^+$ OH$^-$, [cat] = 3.5·10^{-3} mol dm^{-3}. (○) total, (▽) disproportionation, (□) condensation.

tionation products are not changed with the variation of initial substrate and catalyst concentrations, Figs. 4 and

Scheme 3.

5, it may be assumed that both these processes conform to the same kinetic law.

The initial rate kinetics were analysed assuming that the component reactions in the system are first order in the substrate[1]. This assumption was based on previous results for the kinetics of disproportionation of oligosiloxanol in the presence of strong bases [10]. The validity of this assumption was confirmed in the computer simulation approach.

The dependence of initial specific rates on the catalyst concentration for substrate conversion and for the disproportionation and condensation for MDH is presented in Fig. 4. The apparent order in the total substrate conversion is first order to a good approximation and the orders of both component reactions are fairly close to one. The kinetic law for the initial period of the reaction is approached by general Eq. 4. This kinetic law indicates that there is virtually no self-association of the catalyst and no self-association of ionic intermediate, which would lead to a fractional order as the associates usually are unreactive forms of the catalyst [16,18]. The observed order in catalyst does not exclude the ion pair formation, which could be the reactive form of the catalyst.

$$-1/2 \mathrm{d}[MD_nH]/\mathrm{d}t = (k_{\mathrm{disp}} + k_{\mathrm{cond}})[\mathrm{cat}][MD_nH]$$
$$n = 1,\ 2 \tag{4}$$

The dependence of the initial reaction rate on the initial substrate concentration is very complex (Fig. 5) and does not fit to the internal kinetics. The specific rate increases with the decrease of the initial concentration of SiOH. The reason for this strange dependence is the medium effect on the catalytic activity of the base. The nucleophilic reactivity of the naked silanolate ion in a weakly solvating solvent, such as toluene, must be very high. However, the interaction of the silanolate anion with proton donating species, such as silanol and water formed in the condensation, strongly decreases its thermodynamic activity. Interaction of silanol with silanolate, structure 5, reduces the density of negative charge on silanolate, and effectively weakens its nucleophilicity.

$$\tag{5}$$

This phenomenon is not expected to affect the kinetic curves for the reactions in MDH and MD$_2$H systems (Figs. 2 and 3). First, the disproportionation processes do not change the medium effect, as they do not change the total concentration of silanol groups nor it produces

any water. Second, the condensation processes occur in a limited range. Moreover, the ability of water to form complexes with silanolate may be comparable to that of siloxanol. Thus, the replacement of silanol with 1/2H$_2$O, which occurs as the condensation proceeds, may not change the effect of the reaction medium. On the other hand, the condensation of MH is slowed down by water formed in the reaction, Fig. 1. Thus, MH is less effective than water in decreasing the thermodynamic activity of silanolate.

Both component reactions, disproportionation and condensation, conform to the Arrhenius dependence (Fig. 6). Activation parameters are shown in Table 1. Values of the parameters for both reactions are similar. It seems that the energy barrier for the condensation process is similar to that for the disproportionation. Entropies of activation are similar as well.

2.3. Initial kinetics in mixed systems MH + MDH, MH + MD$_2$H and MDH + D$_4$

Kinetic runs were followed using a mixture of MH and MDH which permits the comparison of heterocondensation, MH + MDH, according to Eq. 6, with homocondensation and disproportionation of MDH according to Eq. 7.
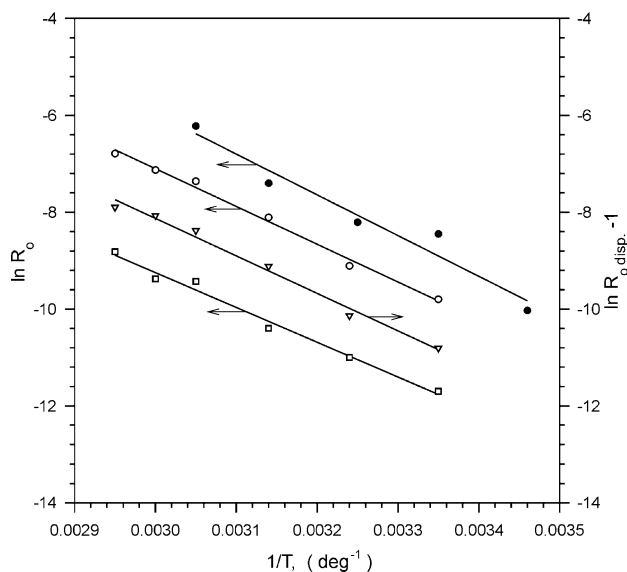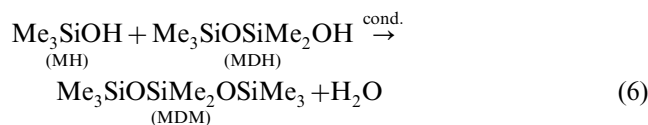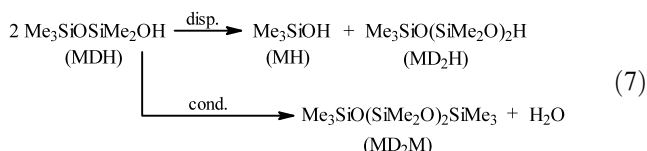
$$\underset{(MH)}{\mathrm{Me_3SiOH}} + \underset{(MDH)}{\mathrm{Me_3SiOSiMe_2OH}} \overset{\mathrm{cond.}}{\rightarrow}$$
$$\underset{(MDM)}{\mathrm{Me_3SiOSiMe_2OSiMe_3}} + \mathrm{H_2O} \tag{6}$$

Fig. 6. Arrhenius plot for condensation and disproportionation of MDH and MD$_2$H in toluene catalysed by [(C$_4$H$_8$)$_3$P–N–P(C$_4$H$_8$)$_3$]$^+$ OH$^-$. For MDH: [cat] = 3.50·10^{-3} mol dm^{-3}, [MDH]$_0$ = 1.52 mol dm^{-3}. (○) substrate conversion, (▽) disproportionation of MDH, (□) condensation of MDH. For MD$_2$H: [cat] = 5.10·10^{-3} mol dm^{-3}, [MD$_2$H]$_0$ = 1.00 mol dm^{-3}, (●) disproportionation of MD$_2$H.

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[1] In some kinetic experiments, first order was observed up to a relatively high conversion, however, it was somehow accidental.

Table 1
Activation parameters for disproportionation and condensation reaction of MD_nH $n = 1, 2$ in toluene, catalysed by $[(C_4H_8)_3PNP(C_4H_8)_3]^+OH^-$

Substrate	Reaction	E_{act} (kcal mol^{-1})	$\Delta H^\ddagger$ (Kcal mol^{-1})	$\Delta S^\ddagger$ (kcal mol^{-1} deg^{-1})
MDH+MDH	Substrate conversion (apparent values)	15.5	14.9	−17.5
	Condensation	14.2	13.6	−26.3
	Disproportionation	15.3	14.7	−18.4
MD₂H+MD₂H	Disproportionation	16.7	16.1	−10.8

$$2\ Me_3SiOSiMe_2OH \xrightarrow{disp.} Me_3SiOH + Me_3SiO(SiMe_2O)_2H \tag{7}$$
$$\text{(MDH)} \qquad\qquad \text{(MH)} \qquad \text{(MD}_2\text{H)}$$
$$\xrightarrow{cond.} Me_3SiO(SiMe_2O)_2SiMe_3 + H_2O$$
$$\text{(MD}_2\text{M)}$$

Unexpectedly, the heterocondensation MH+MDH proceeds faster than the disproportionation of MDH and much faster than the homocondensation of MDH. See Fig. 7 and Table 2.

Similarly, kinetic runs in the system MH+MD₂H gave us an idea about the relative rates of condensation and disproportionation, according to Eqs. 8 and Eq. 9.

$$Me_3SiOH + Me_3SiO(SiMe_2O)_2H \xrightarrow{cond.} Me_3SiO(SiMe_2O)_2SiMe_3 + H_2O$$
$$\text{(MH)} \qquad \text{(MD}_2\text{H)} \qquad\qquad\qquad \text{(MD}_2\text{M)}$$
$$\xrightarrow{disp.} 2\ Me_3SiOSiMe_2OH$$
$$\text{(MDH)} \tag{8}$$

$$2Me_2SiO(SiMe_2O)_2H \xrightarrow{disp.}$$
$$\text{(MD}_2\text{H)}$$
$$Me_3SiOSiMe_2OH + Me_3SiO(SiMe_2O_3H) \tag{9}$$
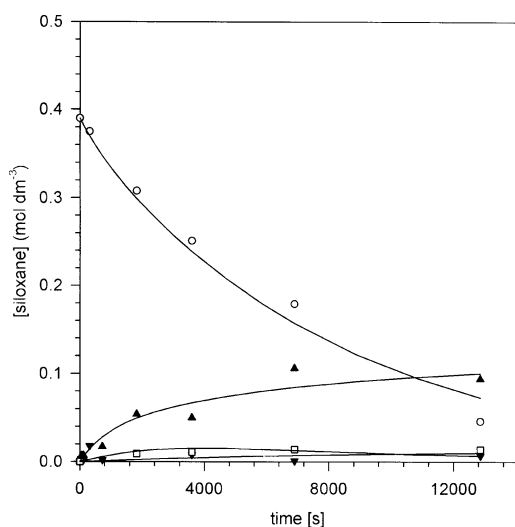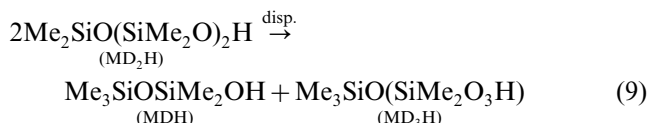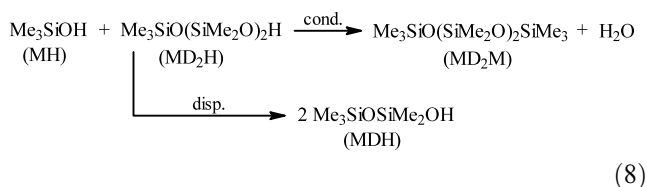$$\text{(MDH)} \qquad\qquad \text{(MD}_3\text{H)}$$

Fig. 7. Simulation of kinetic dependencies (curves) to the best agreement with the data (points) for the condensation and disproportionation reactions in the mixture of MDH and MH in toluene at 25 °C, catalysed by $[(C_4H_8)_3P-N-P(C_4H_8)_3]^+$ OH^-,[cat]₀ = 3.60· 10^{-3} mol dm^{-3}, (○) MDH, (□) MD₂H, (▼) MD₂M, (▲) MDM.

Since initial rates of the formation of MDH and MD₃H are almost the same (Fig. 8), both oligosiloxanols are the products of disproportionation according to Eq. 9. Thus, the dismutation according to Eq. 8 is negligible; consequently, the condensation 8 and disproportionation 9 occur more or less at the same specific initial rates (Fig. 8).

A kinetic experiment was also performed to compare under the same condition the cleavage of the siloxane bond adjacent to the hydroxyl group in MDH with that of an unstrained ring oligomer octamethylcyclotetrasiloxane, D₄. The experiment revealed that D₄ reacts much more slowly (Fig. 9). Considering the statistical factors and initial concentrations the disproportionation is faster than the opening of the D₄ ring by three orders of magnitude, which points to a preferential cleavage of siloxane bonds adjacent to hydroxyl groups by a strong base.

2.4. The simulation of kinetic dependencies

The gas chromatographic method used for studies of siloxanol condensation–disproportionation allows the simultaneous analysis of the concentration of various oligohomologues of the MD_nH and the MD_nM series. This experimental data was used for simulations of concentration–time dependencies for various species to the best agreement with experimental data. This approach provides information for a better understanding of this complex process. In particular, it leads to interpretation of the kinetics of the reaction system at much broader substrate concentration ranges as it accounts for the formation of the second generation of products, Scheme 3.

In the simulations the following assumptions were used. A series of consecutive condensation and disproportionation reactions, Eq. 10, Eq. 11–12, lead to the formation of various MD_nH and MD_nM homologues.
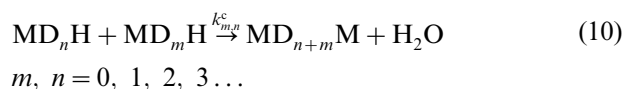
Condensations :

$$MD_nH + MD_mH \xrightarrow{k^c_{m,n}} MD_{n+m}M + H_2O \tag{10}$$
$$m, n = 0, 1, 2, 3 \ldots$$

Table 2
Catalytic constant values, k^1 mol^{-1} s^{-1} dm^{-3}, for disproportionation and condensation of permethyloligosiloxanols in toluene, 25 °C, [SiOH]$_0$ = 1.0 mol dm^{-3}

| Reaction	From simulation				From initial rates			
	Disproportionation $k_{disp.}$	Condensation $k_{cond.}$	System	relative rates $k_{cond.}/k_{cond.\ (MDH)}$	Disproportionation $k_{disp.}$	Condensation $k_{cond.}$	Substrate conversion	Relative rates $k_{cond.}/k_{cond.\ (MDH)}$
MH+MH		0.41 (0.40)	MH+MDH (MH+MD$_2$H)	230		0.46		307
MH+MDH		0.028	MH+MDH	16		0.021	0.022	14
MH+MD$_2$H		0.014	MH+MD$_2$H	7.8	< 0.001	0.015	0.028	10
MDH+MDH	0.013 (0.012)	0.0018 (0.0015)	MDH+MDH (MH+MDH)	1	0.012	0.0015	0.013	1
MD$_2$H+MD$_2$H	0.045 (0.032)	0.0033 (0.0031)	MD$_2$H+MD$_2$H (MH+MD$_2$H)	1.8	0.042	0.003	0.043	2
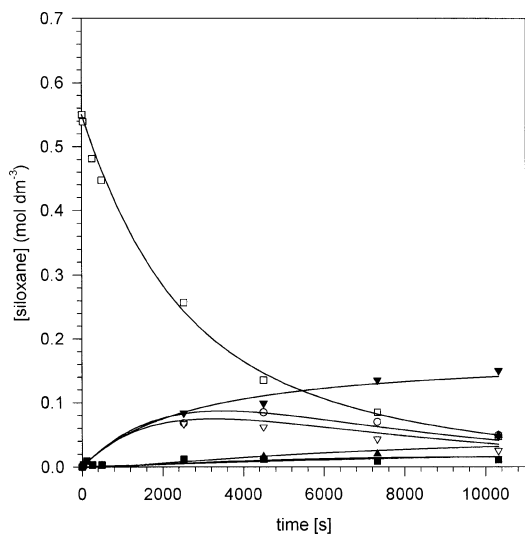
Fig. 8. Simulation of kinetic dependencies (curves) to the best agreement with the data (points) for the condensation and disproportionation reactions in the mixture of MD_2H and MH in toluene at 25 °C catalysed by $[(C_4H_8)_3P-N-P(C_4H_8)_3]^+$ OH^-, $[cat]_0 = 5.10 \cdot 10^{-3}$ mol dm^{-3}, ($\square$) MD_2H, ($\blacksquare$) MD_4M, ($\triangledown$) MD_3H, ($\bigcirc$) MDH, ($\blacktriangledown$) MD_2M, ($\blacktriangle$) MDM.
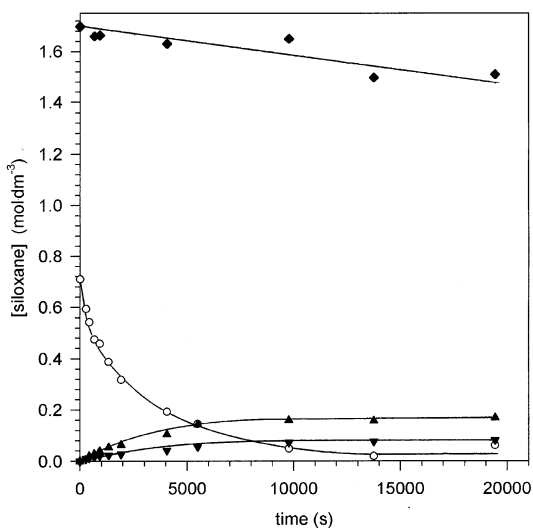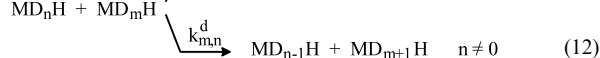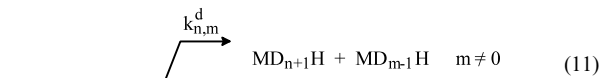

Fig. 9. Competition of condensation and disproportionation of MDH and ring opening of octamethylcyclotetrasiloxane (D_4) catalysed by $[(C_4H_8)_3P-N-P(C_4H_8)_3]^+OH^-$, in toluene, 25 °C, $[D_4]_0 = 1.70$ mol dm^{-3}, $[MDH]_0 = 0.71$ mol dm^{-3}, $[cat]_0 = 5.90 \times 10^{-3}$ mol dm^{-3}. ($\blacklozenge$) D_4, ($\bigcirc$) MDH, ($\blacktriangledown$) MD_2M, ($\blacktriangle$) MDM.

disproportionations:

$$MD_nH + MD_mH \begin{array}{c} \xrightarrow{k^d_{n,m}} MD_{n+1}H + MD_{m-1}H \quad m \neq 0 \quad (11) \\ \xrightarrow{k^d_{m,n}} MD_{n-1}H + MD_{m+1}H \quad n \neq 0 \quad (12) \end{array}$$

All reactions are bimolecular and, according to the mechanism discussed in the next section, they occur

between the neutral, MD_nH, and the negatively charged species MD_m^-. Thus, the following reactions between MD_m^- and MD_nH were taken into consideration (Scheme 4):

Condensation (m, n): $\qquad MD_m^- + MD_nH \xrightarrow{k^c_{m,n}} MD_{m+n}M + OH^-$
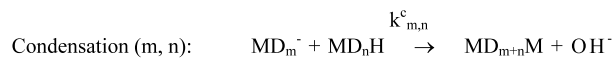
(m,n)		m →		
	(0,0)	(1,0)	(2,0)	(3,0)
n	(0,1)	(1,1)	(2,1)	(3,1)
↓	(0,2)	(1,2)	(2,2)	(3,2)
	(0,3)	(1,3)	(2,3)	(3,3)

Disproportionation: $\qquad MD_m^- + MD_nH \xrightarrow{k^d_{m,n}} MD_{m+1}^- + MD_{n-1}H$
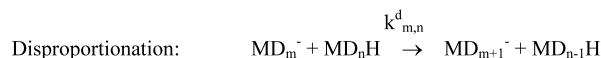
(n,m)		m →		
		(1,1)	(2,1)	(3,1)
n	(0,2)		(2,2)	(3,2)
↓	(0,3)	(1,3)		(3,3)

Scheme 4.

Disproportionation reactions for $n = m+1$ are omitted, since they do not change the concentrations of reactants.

If initial concentration of the base was [B], then the following equations were assumed to hold:

$$[MD^-] + [MD_2^-] + [MD_3^-] + \ldots = [B] \qquad (13)$$

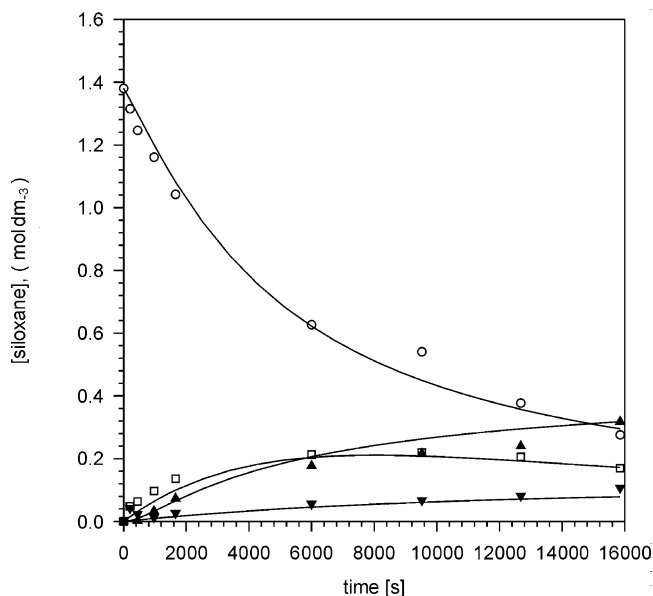Fig. 10. Simulation of kinetic dependencies (curves) to the best agreement with the experimental data (points) for the disproportionation and condensation of MDH in toluene at 25 °C catalysed by $[(C_4H_8)_3P-N-P(C_4H_8)_3]^+OH^-$, $[MDH]_0 = 1.52$ mol dm^{-3}, $[cat]_0 = 6.73 \cdot 10^{-3}$ mol dm^{-3}, ($\bigcirc$) MDH, ($\square$) MD_2H, ($\blacktriangledown$) MD_2M, ($\blacktriangle$) MDM.

$$[MD_i^-] = [B] \frac{[MD_iH]}{\sum\limits_{n=1}[MD_nH]} \qquad (14)$$

Taking into account that the acidity of MH is lower than that of MD_nH, $n \geqslant 1$, $[M^-]$ [22] was omitted in Eq. 13 in the simulation of the kinetics in the systems MDH and MD_2H.

Eq. 13 corresponds to the assumption that the acidity of the siloxanols is large enough to transform all the catalyst introduced to the reaction system into siloxanolates. The assumption is justified by the much higher acidity of oligosiloxanols compared with that of water and alcohols [10]. If this holds, first order with respect to the total SiOH should be observed. The Eq. 14 corresponds to the assumption that the acidity of all MD_nH species are the same, independent[2] of n.

Other assumptions were those concerned with the relative reactivities. Thus, it was assumed that rate constants $k_{n,m}^c$ for all reactions of condensation $n > 2$, $m > 2$ are the same. The same assumption was used for disproportionation process. Thus, it was generally assumed that the reactivity is independent of chain length except for the cases when $n \leqslant 2$, $m \leqslant 2$. Examples of the simulation of both substrates MDH and MD_2H are shown in Figs. 10 and 11. In Table 2 are given the rate constants for the simulations. Simulated dependencies fit well to experimental data confirming the validity of the assumptions in the kinetic analysis of the system.

The rate constants obtained from the simulation correlate well with the catalytic rate constants obtained from the analysis of initial rates confirming the validity of the assumptions of the simulation. This clearly shows that the complex character of the kinetics of the reaction of MDH and MD_2H is not only the result of consecutive reactions but is also due to the variation of the substrate conjugate base concentration with substrate conversion. The substrate competes for the base with products of disproportionation. The first order kinetics assumption is valid only for the initial period of reaction, when the substrate-conjugate base concentration is equal to the total catalyst concentration in the system.
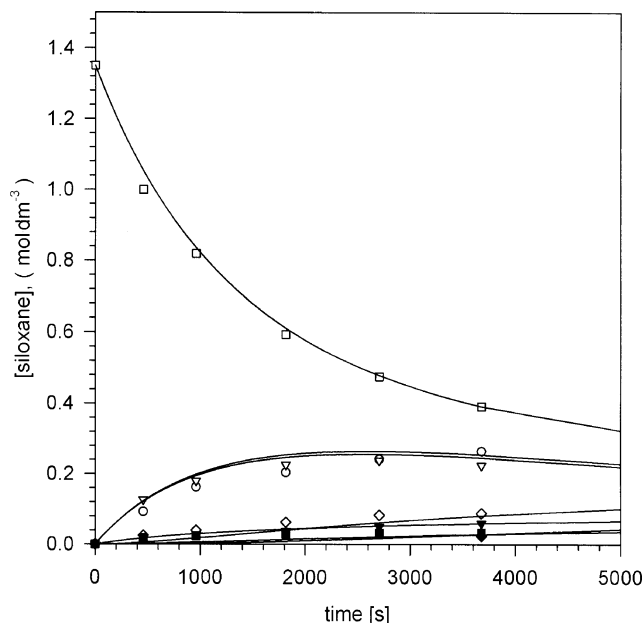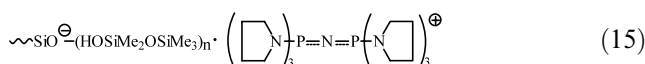

Fig. 11. Simulation of kinetic dependencies (curves) to the best agreement with the experimental data (points) for the disproportionation and condensation of MD_2H in toluene at 25 °C catalysed by $[(C_4H_8)_3P-N-P(C_4H_8)_3]^+$ OH^-, $[MD_2H]_0 = 1.35$ mol dm^{-3}, $[cat]_0 = 6.0 \cdot 10^{-3}$ mol dm^{-3}. (□) MD_2H, (○) MDH, (▽) MD_3H, (◇) MD_4H, (■) MD_4M, (▼) MD_2M.
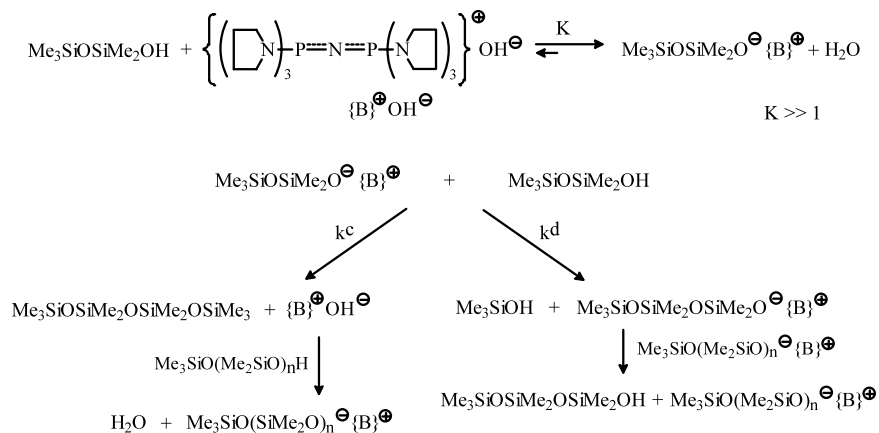
2.5. General mechanism of the reaction

The first order of the reaction in substrate together with the first order in catalyst, the same kinetic law for the condensation and disproportionation, as well as relative rates and activation parameters are rationalised on the basis of a two step mechanism presented in Scheme 5.

Since toluene is a solvent of low dielectric constant, the silanolate must appear as an ion-pair. The charge on the diphosphazenium counter-ion is effectively delocalised and stabilised by six bulky pyrrolidinyl groups at the phosphorus atoms, which should prevent any specific interaction of the phosphazenium ion with the silanolate. Thus, the ion pair is likely to be separated by silanol molecules interacting with the silanolate anionic centre (structure 15). The number of silanol molecules solvating the anionic centre depends on the silanol concentration.

$$\sim\!\!\sim\!\!SiO^{\ominus} \cdot (HOSiMe_2OSiMe_3)_n \cdot \left(\underset{3}{\overset{}{N}} \right)P=N=P\left(N \underset{3}{\overset{}{}} \right)^{\oplus} \qquad (15)$$

The disproportionation is significantly faster than condensation in the MDH and MD_2H series; however, it is not the dominating process. Both competing reactions exhibit very similar activation parameters and the same kinetic law. There is evidence that oligosiloxanol disproportionations and oligosiloxanol condensations occur via a bimolecular transition state.

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[2] This assumption is reasonable for the purpose of the simulation. Taking into account that the acidity of MH is considerably lower than that of other siloxanols of MD_nH series the reaction of M^- is disregarded in the analysis of the MDH and MD_2H reaction systems (the stationary $[M^-] = 0$). However, M^- is taken into consideration in the analysis of the system with trimethylsilanol. The lower stationary concentration of M^- resulting from the lower acidity of MH is partly compensated by its higher nucleophilicity thus the net effect on the contribution of M^- reactions in MD_nH system should not be significant.

Me₃SiOSiMe₂OH + {([N]₃—P=N=P—[N]₃)}⁺ OH⁻ $\xrightleftharpoons{K}$ Me₃SiOSiMe₂O⁻ {B}⁺ + H₂O

{B}⁺ OH⁻   K >> 1

Me₃SiOSiMe₂O⁻ {B}⁺ + Me₃SiOSiMe₂OH

kc ↓   ↓ kd

Me₃SiOSiMe₂OSiMe₂OSiMe₃ + {B}⁺ OH⁻   Me₃SiOH + Me₃SiOSiMe₂OSiMe₂O⁻ {B}⁺

Me₃SiO(Me₂SiO)ₙH ↓   ↓ Me₃SiO(Me₂SiO)ₙ⁻ {B}⁺

H₂O + Me₃SiO(SiMe₂O)ₙ⁻ {B}⁺   Me₃SiOSiMe₂OSiMe₂OH + Me₃SiO(Me₂SiO)ₙ⁻ {B}⁺

Scheme 5.

Nucleophilic attack of the anion requires its desolvation by removal of at least part of the silanol molecules stabilising the anion. The nucleophilic attack is directed to the terminal silicon bearing the hydroxyl group. It is surprising that during this reaction the siloxane bond is more easily cleaved, leading to disproportionation (Scheme 6), than cleavage of the bond to hydroxyl occurs, which would lead to condensation.

It has been shown [10] that the siloxanol disproportionation is favoured when a counter-ion is capable of strongly interacting with silanolate, as the rate of the disproportionation decreases in series of cations $Li^+ > Na^+ > K^+ > Cs^+$. The phosphazenium counter-ion used in the present study only loosely interacts with silanolate, but still the domination of the disproportionation over the silanol condensation is observed.

On the other hand, siloxane acquires the negative charge more easily than hydroxyl and hence makes it a better leaving group. It should also be remembered that the siloxane bond is activated towards cleavage by the adjacent hydroxyl [23]. As shown here, the siloxane bond in octamethylcyclotetrasiloxane (D₄) is opened by the same base much more reluctantly than the terminal bond in the hydroxyl-ended polysiloxane chain. Recent calculations showed that the silanol group, even partially ionised, decreases the energy of the adjacent Si–O bond by both negative hyperconjugation $p(O) \rightarrow \sigma^*(Si-O)$ effect and the $p(O) \rightarrow d(Si)$ orbital interaction effect

[24].These effects are the reason for a great tendency to cleavage of the terminal siloxane bond in polisiloxanols resulting in dismutation.

The initial rate of the substrate conversion changes as follows in the series $MH + MH > MH + MDH > MH + MD_2H > MDH + MDH < MD_2H + MD_2H$, Table 2. This trend is strange and shows that the reactivity is affected by several factors. First, the reaction $MDH + MDH$ and $MD_2H + MD_2H$ may be considered as models of a polymer–polymer reaction which, because of steric reasons, usually occur more slowly than the corresponding polymer–monomer process, the models of which are $MH + MDH$ and $MH + MD_2H$. The reaction between two monomer molecules, model $MH + MH$, is expected to still be faster, which is the case. On the other hand, susceptibility to nucleophilic attack increases in the series $MH < MDH < MD_2H$, but this factor is partly compensated by the reverse order of the nucleophilicity of the anion $M^- > MD^- > MD_2^-$. Thus, the net electronic effect may be less important than the steric effect, although it is manifested in a higher rate of MD₂H reaction as compared with MDH.

Another interesting feature of the kinetics is the fast increase of the contribution of the disproportionation reactions in series $MH + MDH < MH + MD_2H < MDH + MDH < MD_2H + MD_2H$. This observation may be easily understood on the ground of the bimolecular mechanism if structures of pentacoordinate
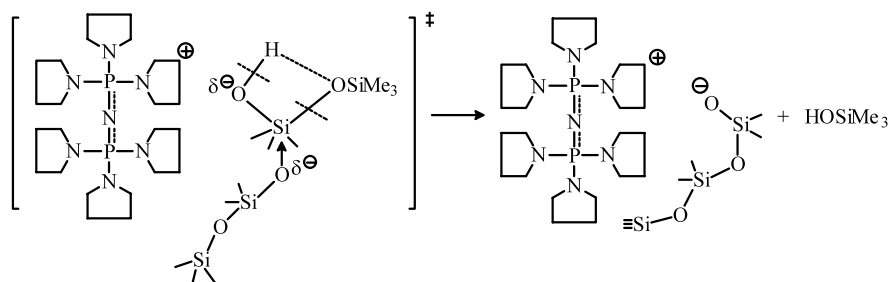
Scheme 6.

silicon transition state, Eqs. 16 and 17, or a pentacoordinate silicon intermediate are considered.

$$(16)$$
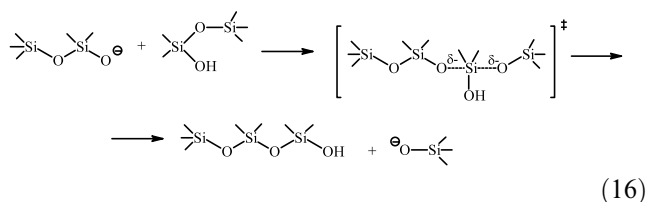
The nucleophilic attack by silanolate anion places the siloxane substituent into the apical position and OH group in the equatorial position. This is not only because silanolate is a better leaving group, more effectively stabilising the negative charge as compared with OH$^-$, but also because the two bulky siloxane substituents at pentacoordinate silicon will tend to occupy positions which are as far from each other as possible. Whereas, the nucleophilic attack on MH always directs the OH group to the apical position, Eq. 17.

$$(17)$$
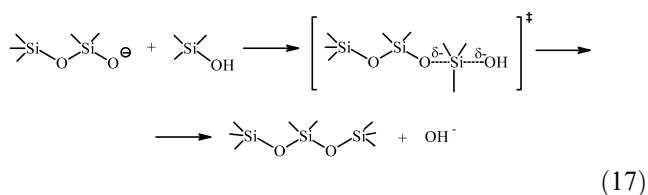
3. Experimental

3.1. Chemicals

Solvents toluene and acetonitrile were purified according to the standard methods described in Ref. [25].

1,1,3,3,3-pentamethyldisiloxane-1-ol (MDH) was synthesised by hydrolysis of 1,1,1,3,3-pentamethyldisiloxane, which had been purchased as reagent grade product of ABCR. The reaction was catalysed by 5% Pd/C (Aldrich) purified by distillation at 52 °C/50 mm Hg. The purity was checked by gas chromatography.

1,1,3,3,5,5,5-heptamethyltrisiloxane-1-ol (MD$_2$H) was synthesised in an analogous way from 1,1,1,3,3,5,5-heptamethyltrisiloxane. MH was synthesised by hydrolysis of hexamethyldisilazane [26] and purified by distillation at 25 °C/50 mm Hg. It contained several percent of hexamethyldisiloxane (MM) which was determined by gas chromatography and regarded in the preparation of solutions for kinetic experiments.

Standards for analysis: linear permethyloligosiloxanes - octamethyltrisiloxane (MDM), decamethyltetrasiloxane (MD$_2$M), dodecamethylhexasiloxane (MD$_3$M) were prepared and purified using well known procedures [27]. Their purity was checked by gas chromatography.

Quenching agent ethyldimethylchlorosilane was synthesised by Grignlard reaction. Ethylmagnesium chloride prepared from 10 g (0.41 mol) of magnesium in 100 ml of dried Et$_2$O was slowly added to 52.9 g (0.41 mol) of dimethyldichlorosilane in 200 ml of dried Et$_2$O. Ethyldimethylchlorosilane was isolated and purified by distillation on column (15 th pl.). Only 15 g fraction (30% yield) boiling at 88 °C was cut rejecting a large primary fraction. The purity of the product checked by gas chromatography was 97%, but the only contamination was Et$_2$Me$_2$Si (about 3%) which did not interfere in analyses in kinetic studies.

3.2. Preparation of catalyst

Hexachlorodiphosphazenium hexachlorophosphate (**1**), was synthesised by reaction of phosphorus pentachloride with ammonium chloride in POCl$_3$ according to the procedure similar to that described in Ref. [28]. It was purified by washing with CH$_2$Cl$_2$ and CCl$_4$ and drying under vacuum 10^{-3} torr at room temperature (r.t.) (yield over 90%).

Compound **1** (6.94 g, 13 mmol) in 50 ml of anhydrous toluene were placed under nitrogen in a flask equipped with a condenser, dropping funnel, stirrer and neutral gas inlet. The mixture was cooled down to -50 °C and 13.9 g (195 mmol) of pyrrolidine with 19.7 g (195 mmol) of triethylamine was added dropwise, during 1 h, stirring the reaction mixture at -50 °C pushing a slight stream of nitrogen through the reactor. The system was allowed to warm to r.t. Then it was heated at $+40$ °C with stirring for 26 h under nitrogen. The precipitate of Et$_3$N·HCl was separated. The main low dark yellow viscous–liquid phase was isolated and after dilution with CH$_2$Cl$_2$ was repeatedly shaken with a small amount of water. Solvents and volatile contaminations were removed by heating at 50 °C under vacuum 10^{-3} torr for 5 h. 1,1,1,3,3,3-hexapyrrolidinyl-1,3-diphosphazenium chloride (**2**) (6.2 g, 11.7 mmol) 90% yield, was obtained. ^{31}P-NMR spectrum showed only one signal at about 2 ppm.

Compound **2** (1.3 g) dissolved in 2 ml of 1:1 V/V methanol–water was filtrated through a column ($l =$ 1000 ml, $d = 18$ mm) packed with strongly anionic resin Dowex 550A OH, using H$_2$O–MeOH 1/1 as an eluent. All operations were performed under nitrogen. Carefully decarbonized methanol and water were used. Methanol and water were removed by heating the catalyst at 100 °C under vacuum 10^{-3} torr for 5 h. Since traces of Cl$^-$ anion were detected in the catalyst, it was subjected to the repeated exchange procedure using freshly regenerated Dowex 550 A OH. Then, 1 ml of pure dioxane was introduced. ^{31}P-NMR disclosed the presence of (Pyr)$_3$PNP(O)(Pyr)$_2$ $\delta = 3.66$ (*d*), 9.09 ppm (*d*). In order to remove this impurity about half of the added dioxane was distilled off under vacuum 10^{-3} torr

for 1 h and 1 ml of toluene was added to the phosphazenium base. The upper liquid phase containing toluene and impurities was removed. New portion of toluene was repeatedly added and removed to wash out the impurity.[3] Then solvents were removed by heating at 50 °C at 10^{-3} torr for 2 h. The phosphazenium base was dissolved in CH_3CN to obtain the catalyst stock solution. The ^{31}P-NMR spectrum showed only one signal at $\delta = 2.46$ ppm. The concentration of the catalyst was determined by ^1H-NMR analysis comparing the intensity of the signal of $(CH_2)_2CH_2NCH_2$ with the signal of CH_3NO_2 added as internal standard. The other method was potentiometric titration with HCl standard water solution.

3.3. Kinetic studies

The reaction was carried out in a glass 10 ml reactor fitted with a three ways stopcock connected to a reservoir with pure nitrogen being at a positive pressure. The reactor was thermostated (± 0.1 °C) and fitted with a magnetic stirrer. After purging the reactor with nitrogen the prepared substrate solution in toluene was placed through the stopcock by means of the precision Hamilton syringe. The solution was thermostated. The zero time sample was withdrawn and the solution of catalyst was introduced by means of a precision Hamilton syringe. The time of initiator addition was considered as the zero time of the reaction. Samples were withdrawn at a suitable time interval by means of the Hamilton syringe. Streaming of the nitrogen through the stopcock prevented the reactor content from any contact with atmosphere during the opening of the stopcock. Samples were immediately quenched by introducing them to the Ependorfer vessels containing the solution of an excess of 1:1 mol–mol mixture of ethyldimethylchlorosilane and triethylamine. The mixture quantitatively silylated the silanol groups. The solution was subjected to the gas chromatographic analysis.

3.4. Analysis

Gas chromatographic analysis was performed with a Hewlett–Packard HP 6890 using TDC detector and HP.1 capillary column HP 190592-023, length 30 m, diameter 0.53 mm, carrier gas He 5 ml min^{-1}, detector temperature 250 °C, injector temperature 250 °C, temperature program: 60 °C isoth. 3 min, 60–240 °C, 10 ° min^{-1}. In studies of $MH + MDH$ and $MH + MD_2H$ systems the conditions of analysis were: temperature program: 40 °C isoth., 6 min, 40–240 °C, 10 ° min^{-1}.

The detector response factor for MD_nM oligohomologue series was determined analysing a solution containing a known amounts of compounds of this series $n = 1$–4 and the standard which was undecane. The detector response factor for homologues of MD_nM^{Et} series was determined by the analysis of solutions in which MD_nM^{Et} were quantitatively synthesised in situ by silylation of known amounts of MD_nH with an excess of $EtMe_2SiCl + Et_3N$ mixture.

The ^1H-NMR analyses and ^{31}P-NMR analyses were performed with Bruker 200 and Bruker 500 spectrometers.

The potentiometric titration analyses were performed using a 721 NET Titrino Methron analyser working with electrode 6.0233.100.

3.5. Computer simulation

Kinetics of copolymerisation were simulated by numerical solving of the approximate differential kinetic equations (Scheme 3) using the Runge–Kutta–Fehlberg procedure [29]. Apparent rate constants were found with the non-gradient Rosenbrock optimisation method, in which the least-squares sum of deviations of the calculated concentrations of both monomers from those found experimentally was minimized [30].

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