Polysiloxanol condensation and disproportionation in the presence of a superacid ☆

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Abstract

Kinetics studies of the condensation of model hydroxyl-terminated oligosiloxanes, pentamethyldisiloxane-1-ol (MDH) and heptamethyltrisiloxane-1-ol (MD$_2$H), catalysed by protic complex of tetrakis(pentafluorophenyl)borate in the toluene solution were performed. The dominating reaction was condensation, which was accompanied by disproportionation of oligosiloxanols. Water released in the condensation forms separate dispersed phase, but the phase separation and the presence of water does not affect the rate of the polycondensation. Both processes, condensation and disproportionation, show analogous kinetic laws being first order in silanol and half order in catalyst. They exhibit also similar values of activation parameters. The kinetics are explained by the formation of a reactive protic complex of silanol with borate being in fast preequilibrium with an unreactive complex including two borate molecules and the silanol molecules. The equilibrium lies to the side of the unreactive borate complex.
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1. Introduction

Polycondensation of silanol groups is a principal route to polysiloxanes which are polymers widely used for the fabrication of variety of silicone materials. Although the reaction has been exploited for about 50 years on the industrial scale there is a great interest in new effective and selective catalysts for this process. Strong protic acids such as H$_2$SO$_4$ [1], CF$_3$SO$_3$H [2], HCl [3], CH$_3$SO$_3$H [4] have been used for this purpose as they induce the polycondensation under mild conditions and can be relatively easily removed from the polymer products (for review see [5–8]). In addition, the acids are tolerated by some functional groups which are reactive towards strong bases, such as SiH and C$_6$H$_5$CH$_2$Cl. Since the catalytic activity in the silanol

polycondensation considerably increases with the increase in acid strength of the catalyst [4–6], some hyperacids seem to be particularly attractive. Tetrakis(pentafluorophenyl)borate has been considered as an anion with an exceptionally high degree of charge delocalisation and extremely low nucleophilicity [9–11]. It has been frequently used in the chemistry of transition metal alkyl and olefin complexes as the counter-ion for highly electrophilic cations [11–13]. It was also exploited in synthesis of the silylenium ion R$_3$Si$^+$ [14] and used in the first successful synthesis of tertiary trisilyloxonium ion [15]. New very reactive arenium cations (Wheland complexes) have recently been isolated and characterized using B(C$_6$F$_5$)$_4^-$ as the counter-ion [16]. Jutzi et al. [17] succeeded in generation and isolation in crystalline form the protonated complex of B(C$_6$F$_5$)$_4^-$ with two molecules of diethyl ether which may be considered as a model of a Brönsted acid conjugated to the perfluorinated tetraphenyl borate anion. The X-ray structure of this complex is known. A strong Brönsted acid is also formed when the silylenium complex Et$_3$Si$^+$–B(C$_6$F$_5$)$_4^-$

is treated by anhydrous HCl [16]. A protic acid derived from the perfluorinated borate was also found to be very effective catalyst of the silanol condensation [18]. Transformation of oligodimethylsiloxanediols into a high molecular weight polymer proceeded very fast at room temperature, without the formation of cyclic products, when a very small amount, at the level of ppm, of the acid was introduced into the α, ω-silanol terminated short chain polydimethylsiloxane (PDMS). Thus, the borate-derived acid is very attractive as the catalyst of the polycondensation of the hydrolysate of dimethylchlorosilane, making possible the generation of high molecular weight PDMS without evoking the ring-opening polymerization step.
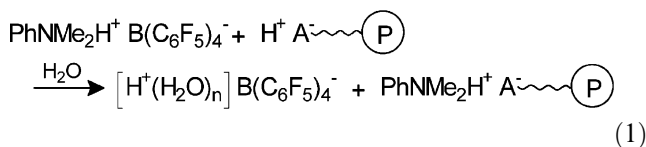
Protonated tetrakis(pentafluorophenyl)borate complex is a superacid gaining distinct advantages over conventional acids used as catalysts for the silanol condensation, as it is a more efficient catalyst and more soluble in non-polar media. Its large anion shows uncommonly small nucleophilicity and exceptional inertness. This feature prompted us to perform kinetic studies of silanol polycondensation catalyzed by a protic tetraperfluorophenylborate complex using a model oligomeric permethylsiloxanols. This system gave us an opportunity to investigate the kinetics and mechanism of the polycondensation, in an acid–base inert, non-polar solvent, such as toluene.

Kinetic studies of acid catalyzed polycondensation of silanols have so far been performed in a polar or weakly polar solvent, such as methylene chloride [1–5] which affect the course of the reaction. The model substrates and analytical procedure used allowed us to explore the competition between the polysiloxanol condensation and the polysiloxanol disproportionation reactions.

2. Results and discussion

2.1. Description of the model systems

The catalyst was obtained by cation exchange in dimethylanilinium tetrakis(pentafluorophenyl)borate on an acid ion-exchange resin according to the following simplified equation

$$PhNMe_2H^+ \ B(C_6F_5)_4^- + \ H^+ \ A^{\sim\!\sim\!\sim} \ \textcircled{P}$$

$$\xrightarrow{H_2O} \ \left[H^+(H_2O)_n\right] B(C_6F_5)_4^- \ + \ PhNMe_2H^+ \ A^{\sim\!\sim\!\sim} \ \textcircled{P}$$

$$\tag{1}$$

The solvent used in the ion-exchange procedure was ethanol–water 1:1 w/w, but after the exchange it was replaced by acetonitrile. The ^{1}H NMR spectrum of the borate after the ion-exchange showed no anilinium ion signals indicating that full exchange of this ion occurred. ^{19}F NMR spectra of the dimethylanilinium salt and the
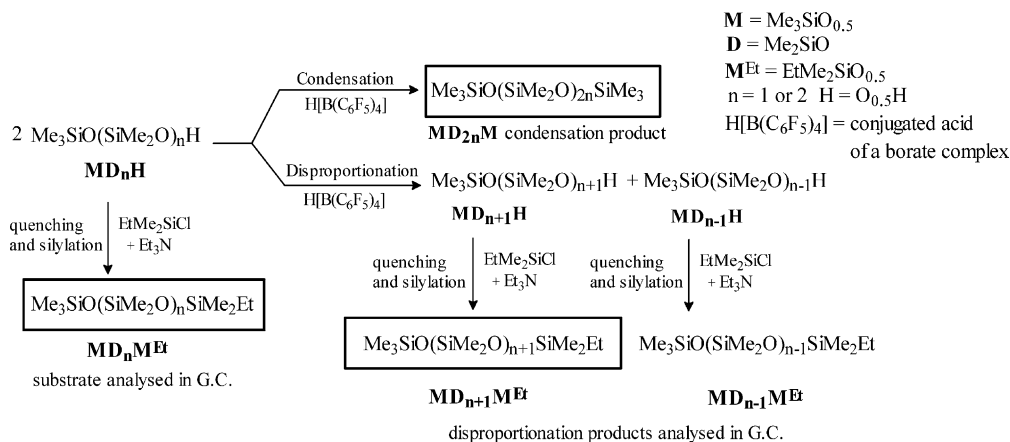
exchange products were virtually the same thus indicating that borate anion structure is fully preserved and the proton is not localized on any fluorine atom on the ^{19}F NMR time scale. It appears that the protonated solvent species is only loosely bonded to the anion. However, it is also possible that a fast exchange of proton between fluorine–$H^+(H_2O)_n$ structures occurs. The ^{1}H NMR spectrum of the acid complex in acetonitrile shows no signal due to ethanol, but shows a single proton signal located about 5.4 ppm, it is assumed that the complex contains coordinated water molecules.

The model substrates and techniques used in the kinetic studies were similar to those used by us in studies of the kinetics of the disproportionation–condensation of oligosiloxanols in the presence of a superbase [19]. The model is presented in Scheme 1. Pentamethyldisiloxane-1-ol (MDH) and heptamethyltrisiloxane-1-ol (MD$_2$H) were used as models of polysiloxane chain terminated with the OH group. The short symbols used here may lead to confusion, as, according to common convention, $M = Me_3SiO_{1/2}$ and $D = O_{1/2}Me_2SiO_{1/2}$. Thus, the above siloxanols should be named $MDO_{1/2}H$ and $MD_2O_{1/2}H$. For the sake of simplicity, we decided to use symbols MDH and MD$_2$H, although they are not perfectly correct. This nomenclature has been used in many previous papers. In the presence of a protic acid two competing reactions of MD_nH, $n = 1, 2$, may occur: silanol condensation leading to $MD_{2n}M$, $n = 1, 2$, and disproportionation affording $MD_{n+1}H + MD_{n-1}H$ oligosiloxanols [4]. All these products are determined by the gas chromatography. Silanol products must be silylated for this analysis. $EtMe_2SiCl$ is used as the silylating agent, instead of simpler Me_3SiCl, to distinguish between the condensation and disproportionation products. This technique permitted kinetics of both processes to be followed. The over-all process is complex, as the disproportionation products $MD_{n+1}H$ and $MD_{n-1}H$ undergo further condensation and disproportionation reactions leading to secondary products. The kinetic analysis was performed under the assumption that in the initial state of the reaction the primary reactions presented in Scheme 1 occur in the absence of the consecutive processes. Thus, it was assumed that balance equations (2) and (3) hold for reactions of respective silanols which, to a fairly good approximation, was the case up to above 50% of the substrate conversion (see Fig. 1).

$$[MDH]_0 = [MDH] + 2[MD_2H] + 2[MD_2M] \tag{2}$$

$$[MD_2H]_0 = [MD_2H] + \frac{1}{2}[MDH] + \frac{3}{2}[MD_3H]$$
$$+ 2[MD_4M] \tag{3}$$

This approach was verified by computer simulation which permitted the extension of the kinetic analysis to include some secondary reactions.

$\mathbf{M} = Me_3SiO_{0.5}$
$\mathbf{D} = Me_2SiO$
$\mathbf{M^{Et}} = EtMe_2SiO_{0.5}$
$n = 1$ or 2 $H = O_{0.5}H$
$H[B(C_6F_5)_4] =$ conjugated acid
  of a borate complex

$2\ Me_3SiO(SiMe_2O)_nH$
MD$_n$H

Condensation $H[B(C_6F_5)_4]$ → $\boxed{Me_3SiO(SiMe_2O)_{2n}SiMe_3}$
MD$_{2n}$M condensation product

Disproportionation $H[B(C_6F_5)_4]$ → $Me_3SiO(SiMe_2O)_{n+1}H + Me_3SiO(SiMe_2O)_{n-1}H$
MD$_{n+1}$H **MD$_{n-1}$H**

quenching and silylation | EtMe$_2$SiCl + Et$_3$N

$\boxed{Me_3SiO(SiMe_2O)_nSiMe_2Et}$
MD$_n$M^{Et}
substrate analysed in G.C.

quenching and silylation | EtMe$_2$SiCl + Et$_3$N   quenching and silylation | EtMe$_2$SiCl + Et$_3$N

$\boxed{Me_3SiO(SiMe_2O)_{n+1}SiMe_2Et}$ $Me_3SiO(SiMe_2O)_{n-1}SiMe_2Et$
MD$_{n+1}$M^{Et}   **MD$_{n-1}$M^{Et}**
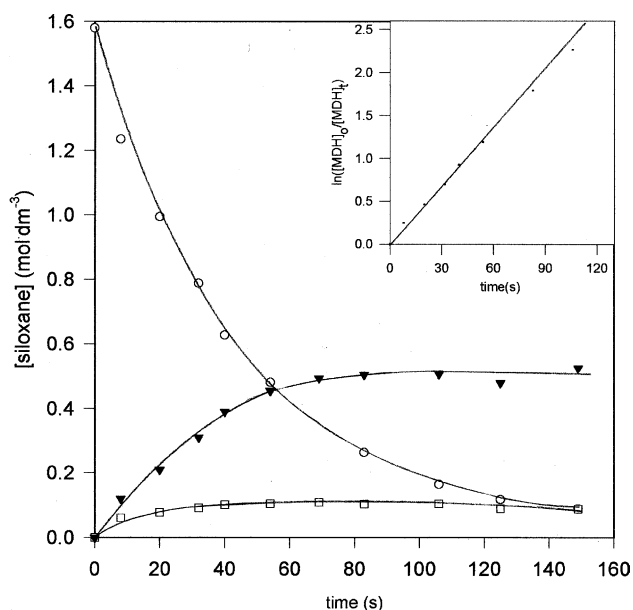disproportionation products analysed in G.C.

Scheme 1.

Fig. 1. The conversion–time dependence and the primary product formation dependencies for the condensation–disproportionation reaction of pentamethyldisiloxane-1-ol, MDH, in toluene catalysed by the tetrakis(pentafluorophenyl)borate protic complex; 25 °C, [HB-$(C_6F_5)_4] = 9.60 \times 10^{-3}$ mol dm^{-3}; (○) MDH (substrate); (▼) MD$_2$M (condensation product); (□) MD$_2$H (disproportionation product).
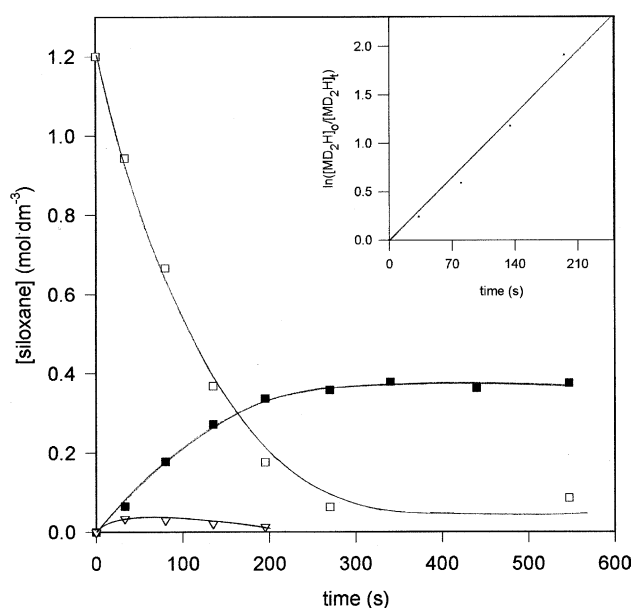

Fig. 2. The conversion–time dependence and the primary product formation dependencies for the condensation–disproportionation reaction of heptamethyltrisiloxane-1-ol, MD$_2$H in toluene catalysed by the tetrakis(pentafluorophenyl)borate protic complex; 25 °C, [HB-$(C_6F_5)_4] = 3.40 \times 10^{-3}$ mol dm^{-3}; (□) MD$_2$H (substrate); (■) MD$_4$M (condensation product); (▽) MD$_3$H (disproportionation product).

2.2. Kinetic results

Example of kinetic runs for MDH and MD$_2$H are presented in Figs. 1 and 2, respectively. The substrate conversion–time plot approaches the first order internal kinetic dependence. Primary products of condensation and disproportionation appear in parallel. Contrary to results of the kinetic studies of MDH and MD$_2$H reactions in basic catalyst systems [19] the condensation here is the dominating process. This is in agreement with earlier studies of the polycondensation in the presence of classical protic acids in methylene chloride [4].

At the beginning the reaction occurred in one phase, however, as the reaction proceeded water produced in the condensation formed a separate dispersed phase. This water does not seem to seriously affect the reaction rate. A separate experiment was performed using toluene solvent saturated with water. No difference in the rate was observed in comparison with the run performed under the same conditions using dried toluene (Table 1). Stirring of the reaction mixture had no significant influence on the reaction rate (Table 1). Thus it was assumed that the reaction proceeds in the organic phase and water forming the separate phase does not affect the catalyst concentration. This observation is in contrast to the results of kinetic studies of the condensation of oligosiloxanediols in the presence of CF$_3$SO$_3$H in methylene chloride [20] which was strongly inhibited by the

Table 1
Specific rate of the conversion of MDH in the presence of tetrakis(pentafluorophenyl)borate protic complex under different conditions

No.	Temperature (°C)	[MDH] (mol/dm^3)	[HB(C$_6$H$_5$)$_4$] (mol/dm^3)	k (s^{-1})
With stirring	24.9	1.54	3.48×10^{-3}	0.028
Without stirring	24.9	1.57	3.46×10^{-3}	0.029
Toluene/H$_2$O	25.0	1.54	3.52×10^{-3}	0.025
Catalyst/MeCN	24.9	1.56	1.68×10^{-3}	0.016
Catalyst/MeOH	25.0	1.56	1.68×10^{-3}	0.014

water formed. A break down of the reaction was observed at the moment of the formation of the separate water phase in those systems. This difference in behaviour of both acids is attributed to a better solubility in organic phase of the borate proton complex compared to triflic acid. However, if *n*-hexane was used as the solvent instead of toluene considerable decrease of the reaction rate was observed, which may be due to a low solubility of the catalyst in this solvent. The solubility of the catalyst in toluene, although much better than in *n*-hexane was not enough to prepare a concentrated stock solution of the catalyst in this solvent. Thus, the catalyst was introduced to the reaction system as a solution in acetonitrile. Small amounts of acetonitrile in the reaction mixture had little influence on the reaction rate. The reaction proceeded at similar rate if acetonitrile was replaced by methanol (Table 1).

The both condensation and disproportionation reactions exhibit the same complex dependence of the rate on the catalyst concentration (Fig. 3). In the range of lower catalyst concentration, below 10^{-3} mol dm^{-3}, the rate of the MDH conversion is proportional to the square root of the catalyst concentration. However, at higher concentrations the exponent becomes lower. For the total conversion of MD$_2$H in the range 1.5–11×10^{-3} the exponent is 0.24.

Since the initial rates of disproportionation and condensation change in the same way with changing catalyst and substrate concentrations the kinetic law for the initial period of the reaction can be expressed by the following equation:

$$\frac{-d[MD_nH]}{dt} = (k_c + k_d)[MDH], \quad (4)$$

where k_c and k_d are first-order rate constants for condensation and disproportionation, respectively. For [HB(C$_6$F$_5$)$_4$] < 10^{-3} we may write Eq. (5), where k_c' and k_d' are respective catalytic constants.

$$\frac{-d[MD_nH]}{dt} = (k_c' + k_d')[HB(C_6F_5)_4]^{1/2}[MDH]. \quad (5)$$

As it might be expected, the internal kinetics of the substrate conversion does not correspond to the observed dependence of the specific rate on the initial substrate concentration. The dependence is complex (Fig. 4) and it mainly reflects the medium effect on the activity of catalyst. Although at higher silanol concen-
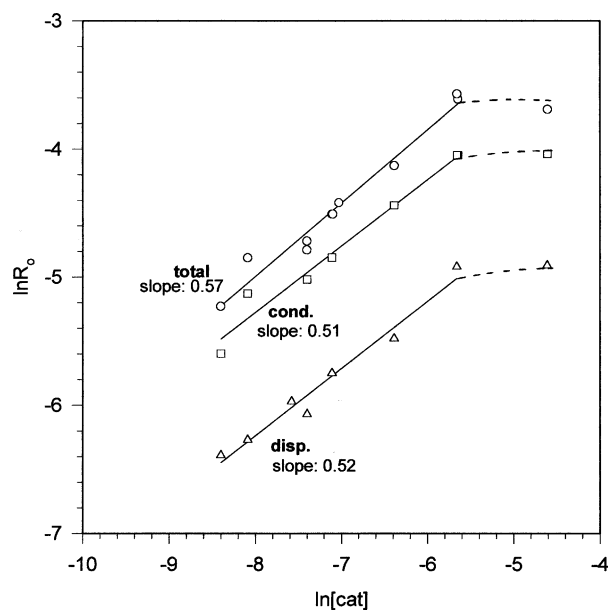

Fig. 3. The dependence of the initial specific rate of the substrate conversion and the product formation on the catalyst concentration in the reaction of MDH in toluene; 25 °C [MDH]$_0$ = mol dm^{-3} catalysed by B(C$_6$F$_5$)$_4^-$ protic complex; (O) MDH conversion; (□) MD$_2$M (the condensation product) formation; (△) MD$_3$H (the disproportionation product) formation.

tration ([MDH]$_0$ > 1 mol dm^{-3}) the specific rate is little dependent on the initial concentration of MDH, in agreement with Eq. (4), however, at concentration below 0.8 mol dm^{-3} the specific rate significantly increases with the decrease of [MDH] (Fig. 4).

The energies and entropies of activation for MDH condensation and disproportionation (Table 2) were determined in a series of experiments at variable temperatures. Both competing reactions show similar values for their respective activation parameters. The negative values of about -30 cal mol^{-1} deg^{-1} for the activation entropy are as expected for bimolecular reactions. Higher reactivity towards condensation is reflected in a slightly lower activation energy for this reaction compared to disproportionation.

In order to verify the kinetic law and to extend the kinetic analysis to some of the consecutive reactions, computer simulations of the substrate conversion and product formation dependencies were performed to best agreement with the experimental data. In the first approach the kinetic curves were simulated on the assumption that the condensation and disproportionation
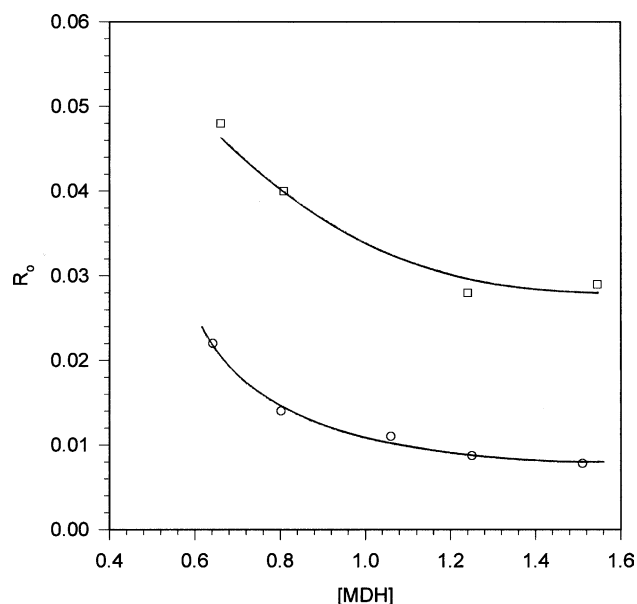
Fig. 4. The dependence of the initial specific rate of the substrate conversion on the initial substrate conversion for MDH in toluene catalysed by $B(C_6F_5)_4$ protic complex at 25 °C; ($\square$) $[HB(C_6F_5)_4] = 3.5 \times 10^{-3}$ mol dm^{-3}; ($\bigcirc$) $[HB(C_6F_5)_4] = 3.05 \times 10^{-3}$ mol dm^{-3}.

Table 2
Values of activation parameters for rearrangement–condensation system of MDH in toluene in the presence of tetrakis(pentafluorophenyl)borate protic complex

	$\Delta E_{act}^{\ddagger}$ (kcal/mol)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal/(mol deg))
Total[a]	11.3	11.1	−28.4
Condensation	10.1	9.7	−34.2
Disproportionation	11.9	11.3	−29.6

[a] From kinetics of the substrate (MDH) conversion.

reactions are of second order in substrate, as indicated from the reaction molecularity. However, this procedure always led to considerable deviations between dependencies simulated and those experimentally measured. On the other hand, the simulations based on the first order equation kinetics fitted fairly well to experimental data (Figs. 5 and 6), thus confirming that the condensation and disproportionation of oligosiloxanols in this system are of the apparent first order in the substrate.

To be consistent with first order in substrate we assumed that the reaction occurs between a silanol molecule and a complex of silanol and catalyst. The concentration of the latter is independent of the silanol concentration because all the catalyst appears in this complex. The observed order in catalyst close to 1/2 may be understood if the catalyst-silanol complex exists in two forms, i.e. unassociated complex being the active intermediate and a self-associated form unable to catalyse the condensation. The equilibrium between them lies well on the side of the inactive form
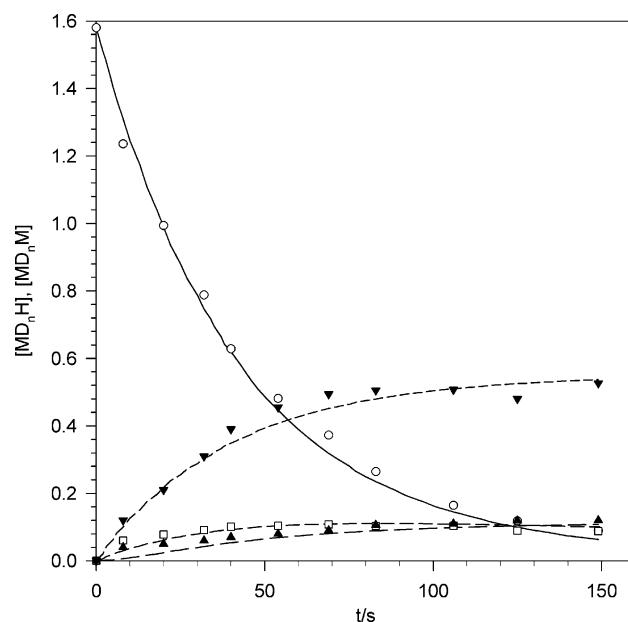

Fig. 5. The simulation of kinetic dependencies (lines) fitting to experimental results (points) for the condensation–disproportionation reaction of MDH in toluene 25 °C; $[HB(C_6F_5)_4] = 9.6 \times 10^{-3}$ mol dm^{-3}. ($\bigcirc$) MDH; ($\blacktriangledown$) MD$_2$M; ($\square$) MD$_2$H; ($\blacktriangle$) MDM.
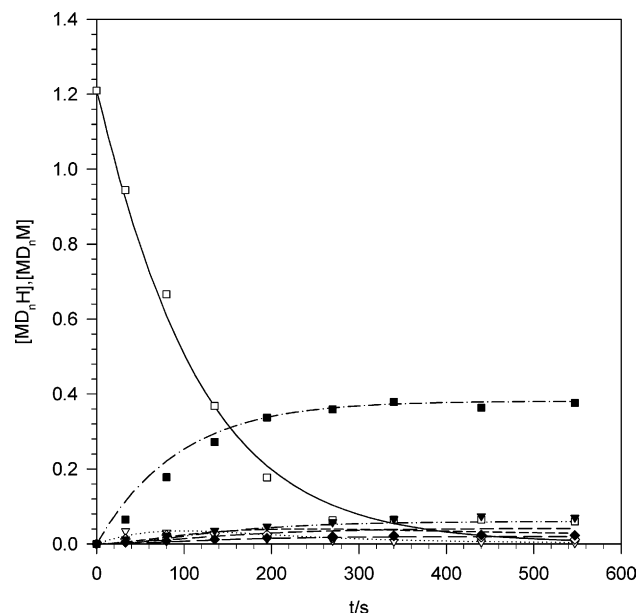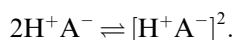

Fig. 6. The simulation of kinetic dependencies (lines) fitting to experimental results (points) for the condensation–disproportionation reaction of MD$_2$H in toluene, 25 °C, $[HB(C_6F_5)_4] = 3.40 \times 10^{-3}$ mol dm^{-3}, ($\square$), MD$_2$H; (—·—■) MD$_4$M; (···▽) MD$_3$H; (−··−▼) MD$_2$M; (---◇) MD$_4$H; (− − ◆) MD$_3$M.

$$2H^+A^- \rightleftharpoons [H^+A^-]^2.$$

At the beginning of the reaction the substrate is the sole silanol in the system. However, as the reaction proceeds, other silanols are formed and compete for the

catalyst. Thus, to interpret the more complex kinetics at higher conversion we assumed that the concentration of the catalyst–silanol substrate (MD_mH) complex is proportional to the ratio of the substrate concentration to the total silanol concentration. Consequently, the concentration of the active form of the catalyst–silanol complex is proportional to the square root of this ratio. Thus, for each elementary reaction of condensation and disproportionation of $MD_mH + MD_nH$, the kinetic equation takes the form:

$$\frac{-d[MD_nH]}{dt} = k\sqrt{\frac{[kat]_0[MD_mH]}{[SiOH]}}[MD_nH]. \tag{6}$$

Some rate constants found by the computer simulation are compared with those from the initial rate determination in Table 3 as well as rate constants calculated by the simulation method for some of the secondary reactions. The data show that the consecutive condensation reactions with the participation of trimethylsilanol MH occur very fast in this system and they account for the relative fast formation of the products of the MD_nM series.

2.3. Mechanism of the condensation–disproportionation process

The similarity in kinetics for the condensation and disproportionation of oligosiloxanols reflects the similarity in their mechanisms. They may occur according to general Eq. (7). The intermediate in both these reactions is a Brönsted acid complex of the borate and silanol.

its protonation may compete with the protonation of the OH group. The cleavage of this siloxane bond may occur as a consequence of its protonation under nucleophilic attack at the terminal silicon atom. The protonated siloxy group is a very good living group as is the protonated hydroxyl group. The higher rate of condensation to disproportionation merely reflects the difference in basicity of both oxygen centres towards the catalyst, which is a proton-donor in the reaction system.

The first order of the reaction in substrate and fractional order in catalyst (Eq. (4)) requires additional comment. The protonated borate complex in acetonitrile most probably appears as a complex with residual water because the nitrilium cation is extremely strong acid and its formation in this system is improbable. The siloxanol substrate have the basicity comparable to that of water [2] and, since it appears in high concentration, all protonated borate may become bonded into a complex with siloxanol when the catalyst is introduced to the substrate solution. Consequently, the concentration of the protonated siloxanol intermediate is little dependent on the substrate concentration which leads to the order in substrate lower than that expected from the reaction molecularity. In the weakly polar medium, in which the process occurs, ion-association phenomena take place. The observed order of 1/2 in catalyst, decreasing on higher catalyst concentration, suggest that protonated siloxanol is complexed with two or more borate anions, possibly via the O–H···F–C hydrogen bonding. Such bonding was found previously, for example, in the anion $[(C_6F_5)_3B(H_3O_2)B(C_6F_5)_3]^-$ [23]. This species is in

$$\tag{7}$$
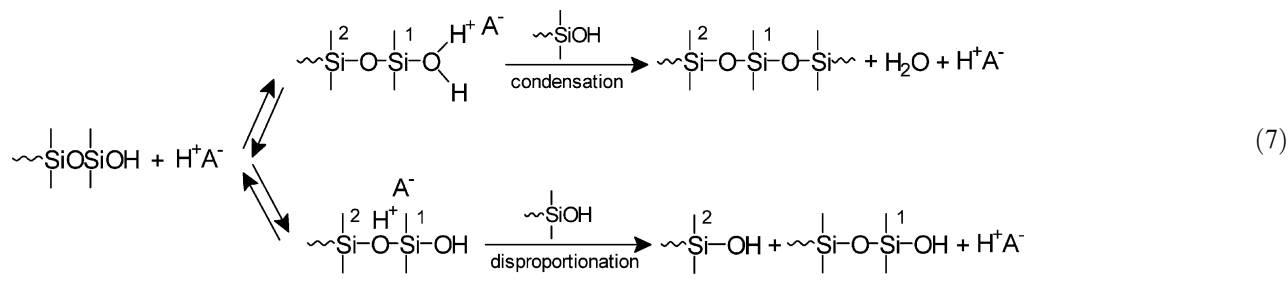
Recent ab initio calculations [21,22] showed that the oxygen atom of the terminal siloxane group adjacent to the hydroxyl group is more basic that other siloxane oxygen atoms in the polysiloxane chain and

equilibrium with a small amount of a monoborate complex that is the true substrate conjugated acid intermediate. The condensation and disproportionation proceeds according to equations (8):
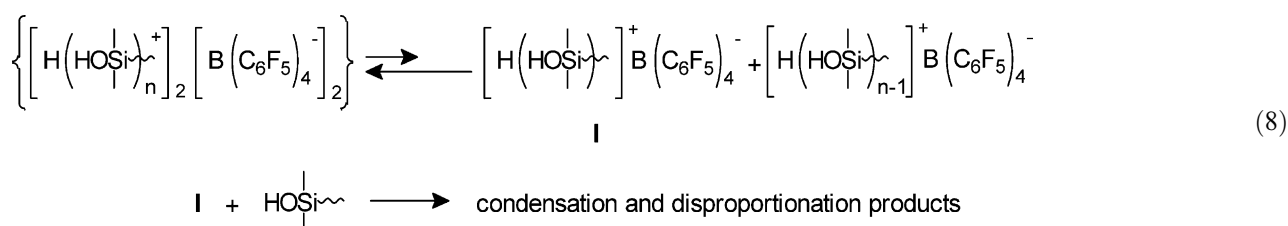

$$\tag{8}$$

I + HOSi~ → condensation and disproportionation products

Table 3

Comparison of the specific rates (apparent first order rate constant $k = k_{cond}$ or $k = k_{disp}$) with corresponding parameters obtained from simulations $k_1 = k\sqrt{\frac{[kat]_0[MD_mH]}{[SiOH]}}$ for component reactions which occur in the solution of pentamethyldisiloxane-1-ol (MDH) and heptamethyltrisiloxane-1-ol (MD$_2$H) in toluene at 25 °C catalyzed by tetrakis(pentafluorophenyl)borate protic complex

Reaction	k (s^{-1})					
	$[MD_nH]_0 = 1.2$ mol dm^{-3} $[HB(C_6F_5)_4]_0 = 3.5 \times 10^{-3}$ mol dm^{-3}			$[MD_nH]_0 = 1.6$ mol dm^{-3} $[HB(C_6F_5)_4]_0 = 9.7 \times 10^{-3}$ mol dm^{-3}		
	n	Exp.	Simul.	n	Exp.	Simul.
$2MD \rightarrow MH + MD_2H$	1	0.022	0.027	1	0.023	0.025
$2MDH \rightarrow MD_2M + H_2O$	1	0.11	0.13	1	0.065	0.088
$2MD_2H \rightarrow MDH + MD_3H$	2	0.0038	0.0076	2	0.0039	0.0049
$2MD_2H \rightarrow MD_4M + H_2O$	2	0.03	0.046	2	0.021	0.022
$MDH + MH \rightarrow MDM + H_2O$	1		1.8	1		1.2
$MD_2H + MH \rightarrow MD_2M + H_2O$	2		2.2	2		2.0
$MDH + MD_2H \rightarrow MD_3H + H_2O$	1		0.068	1		0.03
	2		(0.090)	2		(0.046)

The condensation reaction is faster than the disproportionation, which reflects the difference in the stabilities of the protonation products of the geminal oxygens on the terminal hydroxyl bonded silicon atom. The basic assistance of the counter-ion, stabilizing the protonated substrate, is possible [2,4]. The behaviour of MD$_2$H resembles that of the silanol terminated polysiloxane more closely than the behaviour of MDH, as the trimethylsilyl group increases the basicity of neighbouring oxygens [24]. Rates of condensation and, in particular, disproportionation are larger for MDH than for MD$_2$H (Table 3). The relatively high basicity of MH explains very high reactivity of this species towards condensation.

3. Experimental

3.1. Solvents

Toluene was purified by distillation from sodium. Prepurified water was redistilled, acetonitrile and ethanol were purified by distillation from CaH$_2$.

3.2. Model substrates for kinetic studies

Pentamethyldisiloxane-1-ol (MDH) and heptamethyltrisiloxane-1-ol (MD$_2$H) were synthesized according to the description in [19].

3.3. Standards for analysis

Octamethyltrisiloxane (MDM), decamethyltetrasiloxane (MD$_2$M) and dodecamethylhexasiloxane (MD$_3$M) were prepared and purified using well known procedures [19]. Their purity checked by gas chromatography was more than 99.5%.

3.4. Silylating agent

Ethyldimethylchlorosilane (Aldrich) was used as received. Its purity checked by gas chromatography was more than 97%.

3.5. Preparation of catalyst

Dimethylanilinium tetrakis(pentafluorophenyl)borate (0.62 g, 8.56×10^{-4} mol) was dissolved in 25 ml of 1:1 v/v ethanol/water mixture. The solution was placed at the upper part of the column ($l = 500$ ml, $d = 20$ mm) packed with Amberlyst 15 ion-exchange resin by means of syringe. Amberlyst had been conditioned in water and washed repeatedly with purified water (4×100 ml) with 50 ml of 1 N HCl, and again with purified water until eluent became neutral.

The generation of the superacid was performed by passing the salt solution through the column using the H$_2$O–EtOH 1/1 mixture as an eluent. The eluent was analysed by NMR. No signals of dimethylanilinium cation was observed in the ^{1}H NMR after exchange. Ethanol and water were removed by keeping under vacuum of 10^{-3} torr for 4 h at room temperature.

The fluorinated arylborate acid was dissolved in CH$_3$CN to obtain the catalyst stock solution. The concentration of the catalyst was determined by ^{19}F NMR analysis comparing the intensity of the signal of $[(C_6F_5)_4B]^-$ with the signal of CF$_3$-Ph added as internal standard.

3.6. Kinetic studies

Polycondensation of MDH and MD$_2$H were carried out in a glass 20 ml reactor fitted with a three way 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. The prepared solution of monomer MDH or MD$_2$H in toluene was placed through the stopcock by means of Hamilton syringe. The solution was thermostated, the zero time sample was taken. The time of addition of the initiator was considered as the zero time of the reaction. Samples were withdrawn at a suitable time interval by means of a Hamilton syringe. Samples were immediately quenched by introducing them into an Eppendorfer vessel containing the solution of an excess of 1:1 mol/mol mixture of ethyldimethylchlorosilane and triethylamine. The mixture quantitatively silylated the silanol groups which was checked in separate experiments. The solution was subjected to the gas chromatographic analysis.

3.7. Analysis

The gas chromatography analysis was performed with Hewlett-Packard HP 6890 chromatograph using a thermal conductivity detector TDC and HP1 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}. The detector response factors for the MD$_n$M oligohomologue series were determined by the analysis of solutions containing known amounts of compounds of this series $n = 1$–4 and the standard which was dodecane [19]. The detector response factor for homologues of the MD$_n$M^{Et} series was determined by the analysis of solutions in which the MD$_n$M^{Et} compounds were quantitatively generated in situ by the silylation of known amounts of MD$_n$H with an excess of EtMe$_2$SiCl + Et$_3$N mixture. The ^{1}H NMR and ^{19}F NMR analyses were performed with Bruker 200 spectrometer.

### 3.8. Computer simulation

Kinetics of condensation were simulated by numerical solution of the approximate differential kinetic equations (6) using the Runge–Kutta–Fehlberg procedure [25]. Apparent rate constants were found with the non-gradient Rosenbrock optimization method, in which the least squares sum of deviations of the calculated concentrations of both monomers from those found experimentally was minimized [26]. The system of kinetic equations used for simulation was simplified so that only reactions involving the primary (i.e., MD$_n$H, $n = 1, 2$) and secondary (i.e., MD$_m$H, $m = n - 1$ and $n + 1$) products were considered. The sets of chemical equations used for simulation are presented in the Supporting Information.

4. Conclusions

1. The silanol condensation is the dominating reaction in the systems studied. Disproportionation of MDH and MD$_2$H occurs as the competitive reaction exhibiting the same general kinetic law as the condensation.
2. The conversion of silanol occurs as first order process which means that the stationary concentration of the substrate-conjugate acid intermediate is independent of the silanol concentration. This further means that all the acid in the reaction system is complexed by the silanol substrate.
3. The reaction shows order in the borate close to 0.5, which is best interpreted by the formation of unreactive substrate complexes bearing two borate molecules. These complexes are in fast equilibrium with a small fraction of a reactive complex containing one borate molecule, which is the substrate conjugate acid intermediate.
4. The computer simulation method permitted the evaluation of the reactivity of Me$_3$SiOH (MH) formed in the reaction systems by disproportionation. The reactivity of MH in the silanol condensation is relatively high. The reactivity order is as follows:

$$MH + MDH > MH + MD_2H > MDH + MDH$$
$$> MD_2H + MD_2H$$
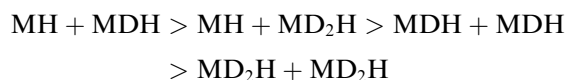
The decreasing reactivity in order MH $\gg$ MDH > MD$_2$H is related to the expected decrease in the basicity of the silanol oxygen.

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