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Disproportionation of oligodimethylsiloxanols in the presence of a protic acid in dioxane *

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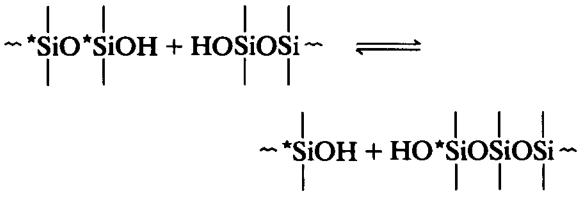
Abstract

The kinetics of the acid-catalyzed disproportionation of α,ω-dihydroxyoligodimethylsiloxanes $HO[SiMe_2O]_nH$, $n = 2, 5$, and their analogues having one hydroxyl function replaced by methyl $Me[SiMe_2O]_nH$, $n = 2, 5$, were studied in dioxane in the presence of water. The formation of the primary disproportionation products was monitored by gas-liquid chromatography. The reaction in dioxane solution can compete with the condensation process only in the presence of water. It is of first order with respect to the substrate, catalyst, and water. The results are interpreted in terms of a stepwise mechanism involving rate determining cleavage of the terminal siloxane unit by water, followed by condensation of transiently-formed dimethylsilanediol with the substrate. The unzipping mechanism involving the dimethylsilanediol intermediate is suggested to operate in hydrolytic cleavage of polydimethylsiloxane exposed to water or water vapour.

1. Introduction

There has recently been considerable interest in the chemistry of oligosiloxanols since they are common intermediates in processes leading to variety of polymers [1,2]. In particular, linear hydroxyl-ended oligodimethylsiloxanes are often used in the synthesis of various types of copolymer [3–6], cross-linked polymer [7,8] or cyclic oligomer [9]. They have also been examined as models for mechanistic studies of the reactions involved in polysiloxane synthesis [10–14]. One of the most intriguing features of these compounds is the unusually high reactivity of the siloxane bond adjacent to the silanol group. It is cleaved much more readily than the other siloxane bonds along the chain [14]. Under certain conditions, the splitting of this bond may compete or even dominate the cleavage of the OH group. As a consequence, the terminal siloxane unit may be transferred from one chain to the end of another chain according to eqn. (1).



$$\sim{}^*\text{SiO}{}^*\text{SiOH} + \text{HOSiOSi}\sim \;\rightleftharpoons\; \sim{}^*\text{SiOH} + \text{HO}{}^*\text{SiOSiOSi}\sim \qquad (1)$$

This specific redistribution leads to disproportionation (dismutation) of an oligosiloxanol. This process was shown to dominate over the polycondensation process in the presence of a strong base [11,12], and may also be a significant side reaction in polycondensation of polysiloxanols in acidic systems [10,15,16].

Knowledge of the specific redistribution involving the terminal units of the siloxane chain is important for understanding the hydrolytic polycondensation of functional silanes. This redistribution contributes also to the ring opening polymerization of cyclic siloxanes since siloxanol end groups always appear in the cationic polymerization of these monomers [17], and may also be present in the anionic polymerization system [18]. For example, the microstructure of the copolymer chain

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comprising siloxane units may depend substantially on the discussed process [18], which may also lead to broadening of the molecular mass distribution [19]. Finally, the chain end redistribution may also account for the behaviour of siloxane polymers since hydroxyl groups often appear at chain ends or may be formed in a polymer degradation process [20].

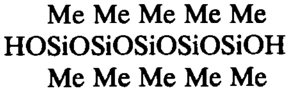
There have been few studies devoted to the specific redistribution of hydroxyl-ended polysiloxanes. Comprehensive kinetic investigations were carried out for the base-catalyzed disproportionation of $Me_3SiOSiMe_2OH$ [12], which threw some light on the mechanism of the redistribution, in the presence of strong bases. The present study was directed towards elucidation of the route taken by this redistribution in acidic media. Some kinetic investigations of the reaction of $Me_3Si(OSiMe_2)_nOH$, $n = 2, 3$, were carried out previously in dioxane in the presence of HCl [16], but only the overall rate constants for the total conversion of the substrate were determined. The kinetic analysis presented in this study is based on the initial rate of formation of the disproportionation product. This approach allows separation of the redistribution reaction of the single species from the condensation reactions and other redistribution processes. Model oligosiloxanols examined include the following:

$\mathrm{HO\overset{Me}{\underset{Me}{Si}}O\overset{Me}{\underset{Me}{Si}}OH}$

1

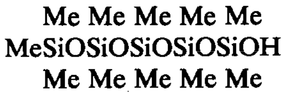
$\mathrm{Me\overset{Me}{\underset{Me}{Si}}O\overset{Me}{\underset{Me}{Si}}OH}$

2



$\mathrm{HO\overset{Me}{\underset{Me}{Si}}O\overset{Me}{\underset{Me}{Si}}O\overset{Me}{\underset{Me}{Si}}O\overset{Me}{\underset{Me}{Si}}O\overset{Me}{\underset{Me}{Si}}OH}$

3



$\mathrm{Me\overset{Me}{\underset{Me}{Si}}O\overset{Me}{\underset{Me}{Si}}O\overset{Me}{\underset{Me}{Si}}O\overset{Me}{\underset{Me}{Si}}O\overset{Me}{\underset{Me}{Si}}OH}$

4

The disproportionation of these oligomers was investigated in dioxane solution with trifluoromethanesulfonic (triflic) acid as the catalyst.

2. Results and discussion

The formation of the disproportionation and condensation products was monitored by sampling, trimethylsilylation (except in the case of **2**), and GLC analysis (Fig. 1).

Competition between oligosiloxanol condensation and disproportionation was found to be strongly affected by the presence of water. In dry dioxane, the

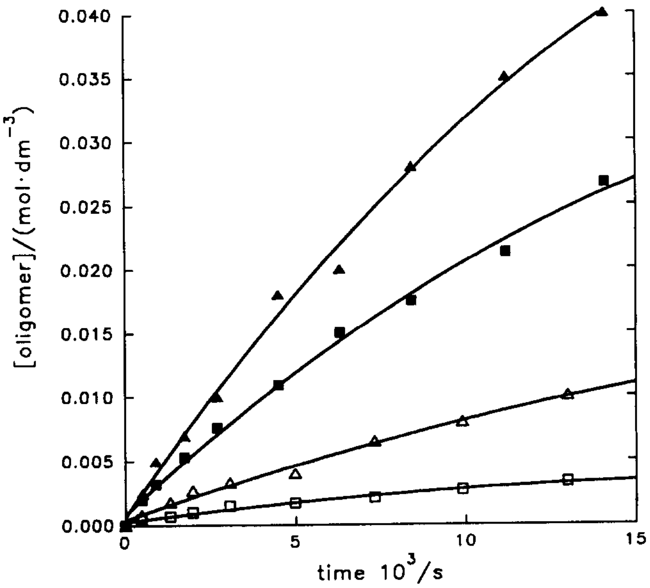


Fig. 1. Conversion-time dependence for the reaction of $Me(Me_2SiO)_2H$ (**2**) in the presence of CF_3SO_3H; $[CF_3SO_3H]_0 = 2 \cdot 10^{-4}$ mol dm^{-3}, $[H_2O]_0 = 1$ mol dm^{-3}, 35°C; disproportionation product $Me(Me_2SiO)_3H$, $[\mathbf{2}]_0 = 0.2$ mol dm^{-3}, △ —— △, $[\mathbf{2}]_0 = 0.6$ mol dm^{-3}, ▲ —— ▲, and the condensation product $Me(Me_2SiO)_3SiMe_3$, $[\mathbf{2}]_0 = 0.2$ mol dm^{-3}, □ —— □, $[\mathbf{2}]_0 = 0.6$ mol dm^{-3}, ■ —— ■.

acid-catalysed disproportionation of oligodimethylsiloxanol seemed not to occur at a significant rate. Thus, almost no disproportionation products were observed in the early stages of the condensation of an oligosiloxanol catalysed by CF_3SO_3H in the initial absence of water. They began to appear in appreciable quantity after a considerable portion of the substrate had been converted and a corresponding amount of water had been formed. For example, in the polycondensation of **3** at an initial substrate concentration of 0.1 mol dm^{-3} the disproportionation was noticeable after about 60% conversion of the diol. However, oligomers formed by disproportionation were observed even after 10% conversion of the diol when its initial concentration was 0.7 mol dm^{-3}.

Considerable disproportionation was observed right from the beginning of the polycondensation process when water was initially introduced into the system. The rate of the disproportionation relative to that of the condensation increased with the water content of the system, as shown in Fig. 2.

The addition of water slows down the overall rate of conversion of the substrate owing to the fall in the proton activity with the increasing water content in

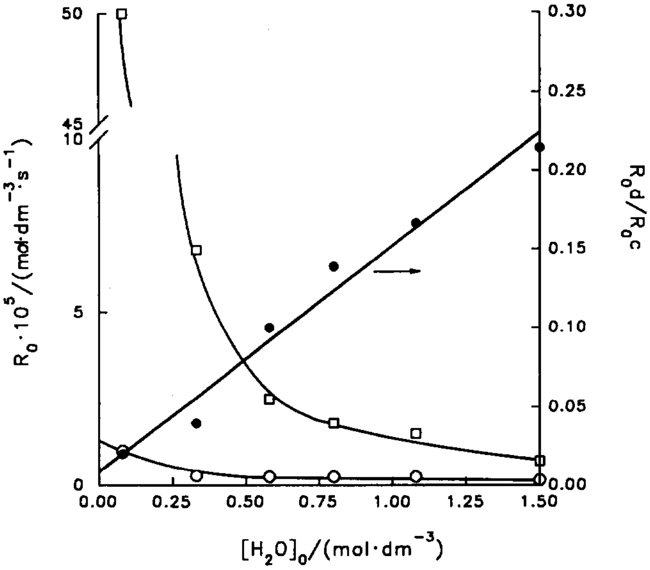


Fig. 2. The effect of water on the initial rate of disproportionation, ○——○, and condensation, □——□ of $HOSiMe_2OSiMe_2OH$ (1) in dioxane in the presence of CF_3SO_3H at 35°C; $[CF_3SO_3H]_0 = 2 \cdot 10^{-4}$ mol dm^{-3}, $[1]_0 = 0.5$ mol dm^{-3}. The ratio of initial rates of disproportionation R_{0d} and condensation R_{0c}, ●——●.

dioxane [21]. This effect of medium shows up strongly in the dependence of the condensation rate on the initial water concentration, as portrayed in Fig. 2.

On the other hand, the apparent effect of water on the rate of the disproportionation is small since the effect of medium is partly compensated by the effect arising from specific participation of water in this reaction. The ratio of initial rates of disproportionation and condensation increases linearly with the initial water content and the slope is close to one. Assuming the effect of medium to be the same for both reactions and water to play no specific role in the condensation, we conclude that the disproportionation is of first order with respect to water. Thus one water molecule is present in the transition state in this reaction.

The initial rate of the disproportionation was determined for systems containing 1 mol dm^{-3} of initially-introduced water. Series of runs were performed for compounds **2** and **4** at various initial concentrations of the substrate and catalyst. Some results are presented in Figs. 3 and 4, where initial rates of disproportionation and intermolecular condensation are compared, and in Fig. 5 which presents a comparison of initial rates for the diol **3** and the related species **4** having one OH group replaced by a methyl group.

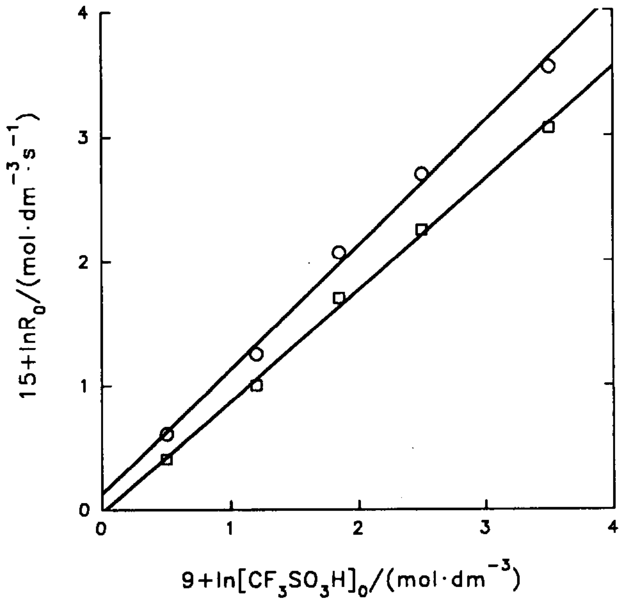


Fig. 3. Comparison of the dependence of the initial rate on the catalyst concentration for the disproportionation, ○——○, and condensation, □——□, of $Me(Me_2SiO)_5H$ (4) in the presence of water at 35°C; $[4]_0 = 0.5$ mol dm^{-3}, $[H_2O]_0 = 1$ mol dm^{-3}.

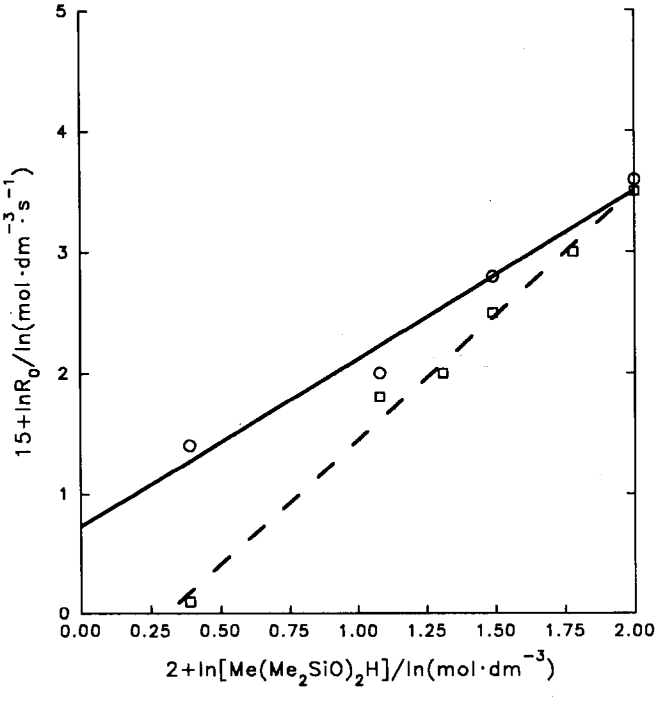


Fig. 4. Comparison of the dependence of the initial rate on the initial oligomer concentration for the disproportionation, ○——○, and condensation, □——□, of $Me(Me_2SiO)_2H$ (2) at 35°C; $[CF_3SO_3H]_0 = 2 \cdot 10^{-4}$ mol dm^{-3}, $[H_2O]_0 = 1$ mol dm^{-3}.

The competing reactions proceed according to eqn. (2).

$$
\begin{aligned}
&2\,\mathrm{HO(SiMe_2O)}_u\mathrm{H}\\
&\quad\xrightarrow{\text{condensation}}\ \mathrm{HO(SiMe_2O)}_{2u}\mathrm{H}\\
&\quad\xrightarrow{\text{disproportionation}}\ \mathrm{HO(SiMe_2O)}_{u-1}\mathrm{H} + \mathrm{HO(SiMe_2O)}_{u+1}\mathrm{H}\\
&2\,\mathrm{Me(SiMe_2O)}_u\mathrm{H}\\
&\quad\xrightarrow{\text{condensation}}\ \mathrm{Me(SiMe_2O)}_{2u-1}\mathrm{SiMe_3}\\
&\quad\xrightarrow{\text{disproportionation}}\ \mathrm{Me(SiMe_2O)}_{u-1}\mathrm{H} + \mathrm{Me(SiMe_2O)}_{u+1}\mathrm{H}
\end{aligned}
\qquad (2)
$$

$u = 2, 5$

The initial rate of the disproportionation process can be approached by eqn. (3).

$$\frac{d[X]}{dt} = k_1[\mathrm{H_2O}]\cdot[\mathrm{CF_3SO_3H}]\cdot[Y]$$

X: product
Y: substrate (3)

The disproportionation rates for all the model oligosiloxanols are listed in Table 1.

The disproportionation process is of first order with respect to the catalyst, and is also, to a fairly good approximation, of first order to the substrate. The kinetic law points to the presence of only one molecule of the substrate in the transition state. This is in contrast to the condensation reaction, which is of second order in the substrate (Fig. 3). Thus, disproportionation must proceed stepwise. The first step is the hydrolytic cleavage of the peripheral siloxane unit leading to the formation of the very reactive dimethylsilanediol, which undergoes a fast condensation with another substrate molecule to give the oligomer with one siloxane unit more than the substrate (eqn. (4)).

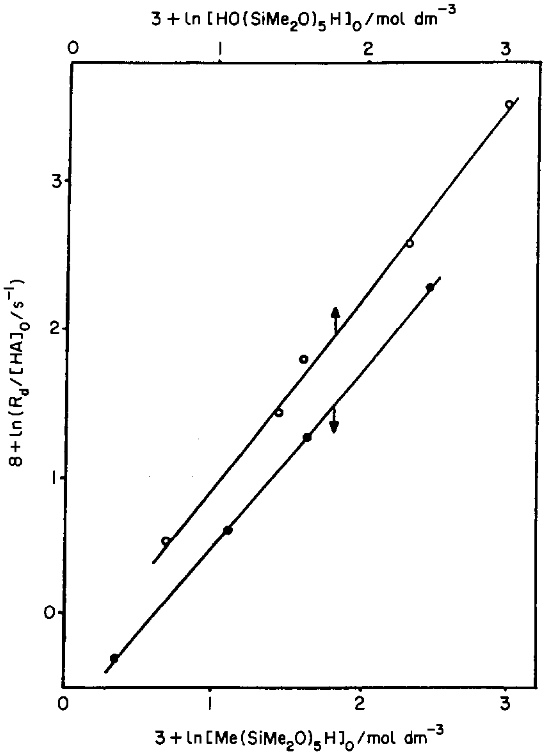
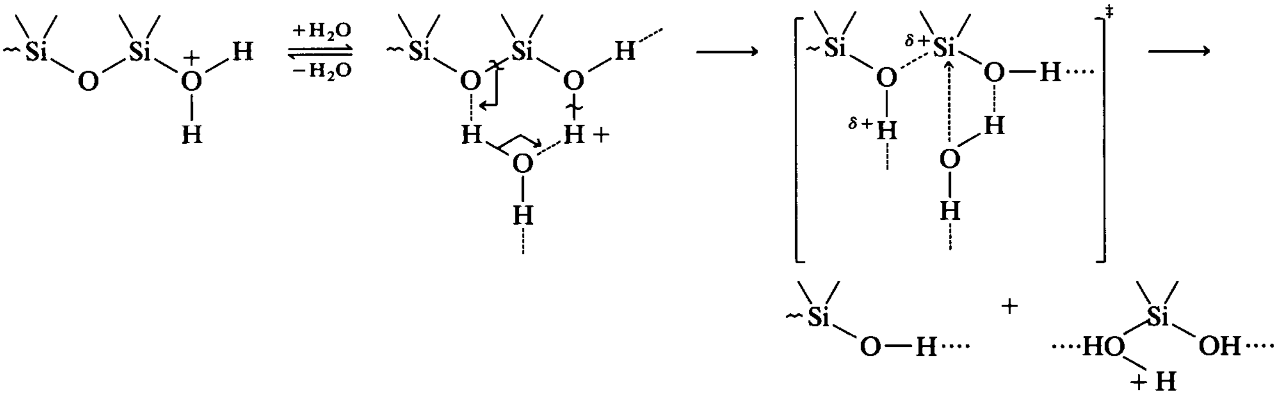


Fig. 5. Dependence of the initial rate on the initial oligomer concentration for the disproportionation of $\mathrm{HO(Me_2SiO)_5H}$ (3), ○——○, and $\mathrm{Me(Me_2SiO)_5H}$ (4), ●——●, at 35°C; $[\mathrm{CF_3SO_3H}]_0 = 2\cdot 10^{-4}$ mol dm^{-3}, $[\mathrm{H_2O}]_0 = 1$ mol dm^{-3}.

$$
\begin{aligned}
&\mathrm{H_2O} + \mathrm{H[OSiMe_2]_5OH} \xrightarrow{\text{slow}} \mathrm{HO[SiMe_2O]_4H} + \mathrm{HOSiMe_2OH}\\
&\mathrm{HOSiMe_2OH} + \mathrm{HO[SiMe_2O]_5H} \xrightarrow{\text{fast}} \mathrm{HO[SiMe_2O]_6H}
\end{aligned}
\qquad (4)
$$

The high susceptibility of dimethylsilanediol towards condensation has been known for a long time. Lasocki



(5)

TABLE 1. Comparison of specific rates of disproportionation of 1–4 in dioxane catalyzed by CF_3SO_3H in the presence of 1.0 mol dm^{-3} of H_2O at 35°C

Substrate		k ($dm^3\ mol^{-1}\ s^{-1}$)		R_d/R_c [a]	
$HO[SiMe_2O]_2H$	**1**	0.025	(0.0125) [b]	0.15	(0.3) [b]
$Me[SiMe_2O]_2H$	**2**	0.032		1.6	
$HO[SiMe_2O]_5H$	**3**	0.014	(0.007) [b]	0.6	(1.2) [b]
$Me[SiMe_2O]_5H$	**4**	0.0065		1.3	

[a] The rate of disproportionation R_d relative to the rate of condensation R_c measured at substrate and catalyst concentrations 0.5 mol dm^{-3} and $2 \cdot 10^{-4}$ mol dm^{-3}, respectively. [b] Taking account of statistical factors of 2 and 4 for disproportionation and condensation, respectively.

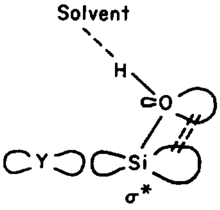
and Chrzczonowicz reported [22] that this compound underwent condensation in acidic dioxane about two orders of magnitude faster than its dimer, *i.e.* tetramethyldisiloxane-1,3-diol.

The hydrolytic cleavage of the terminal siloxane unit is likely to be preceded by the formation of the hydrogen-bonded complex between a water molecule and the protonated siloxanol end group. In this complex, water interacts also with oxygen of the terminal siloxane bond which is to be broken (eqn. (5)).

In such a complex, a proton may be transferred to the siloxane group and this results in cleavage of the siloxane bond. Evidence for protonation of the siloxane oxygen in the neighbourhood of the hydroxyl group is provided by the observation that replacement by the electronegative chlorine atom of the methyl group attached to the penultimate silicon atom lowers the rate of disproportionation more effectively than that of condensation [16]. Thus, in the case of $ClCH_2Me_2SiOSiMe_2OH$, condensation becomes dominant even in the presence of water. Similarly in the present work substrate **1**, having electronegative OH groups at vicinal siloxane units, undergoes disproportionation relatively slowly (Table 1). The reason for this is the lower ease of protonation of the siloxane oxygen in **1** owing to inductive and statistical effects of the other OH group.

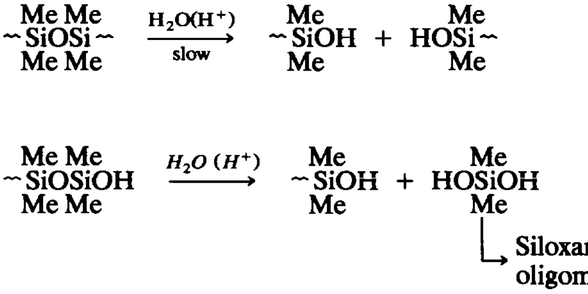
An important role is played by the solvent itself, which, reacting as a base, stabilizes protonated structures. Interaction involving other parts of the siloxane chain, in particular the silanol group at the other side of the chain, does not seem to play any role. The rate of cleavage of **3** is about twice as high as that of **4**, which is closely related to **3** but has only one silanol group. Such difference in the rate is as expected taking into account the statistical factor arising from the presence of two SiOH groups in **3** and only one group in **4**. This factor has a value of 2 for the first order reaction with respect to the substrate.

The unusually high susceptibility of the siloxane bond in the neighbourhood of the hydroxyl substituent as well as a much higher reactivity of monomeric silanediol in the condensation compared with those for any hydroxyl oligomers, must both be related to the anomeric effect of the silanol group [23,24]. The mixing of the orbital occupied by the lone electron pair of oxygen with the empty σ^* orbital of the bond to the leaving group facilitates the title reaction [14,18]. This effect depends strongly upon the amount of negative charge developed on the oxygen atom, and must be enhanced by the hydrogen bond interaction of the silanol group with the dioxan solvent.



(6)

Our results seem to have practical implications. They permit understanding of the behaviour of dimethylsiloxane polymer (PDMS) when exposed to water. The hydrolytic degradation of PDMS is known [20,25] and a promoting role of hydroxyl end groups in this process has been recognized [20]. Although the thermodynamic potential barrier for the reaction of H_2O with PDMS with a trialkylsilyl group at the chain end is thought to be relatively high, the siloxane chain may undergo a slow scission when the polymer is exposed to water, especially when traces of acids or bases are present or the temperature is raised. Once a SiOH end group is present, much faster hydrolytic unzipping of the chain occurs. This depolymerization process produces dimethylsilanediol, which reacts further, possibly to give oligomers, according to eqn. (7).



$$\begin{array}{c}\text{Me Me}\\ \sim\text{SiOSi}\sim\\ \text{Me Me}\end{array} \xrightarrow[\text{slow}]{H_2O(H^+)} \begin{array}{c}\text{Me}\\ \sim\text{SiOH}\\ \text{Me}\end{array} + \begin{array}{c}\text{Me}\\ \text{HOSi}\sim\\ \text{Me}\end{array}$$

(7)

$$\begin{array}{c}\text{Me Me}\\ \sim\text{SiOSiOH}\\ \text{Me Me}\end{array} \xrightarrow{H_2O\,(H^+)} \begin{array}{c}\text{Me}\\ \sim\text{SiOH}\\ \text{Me}\end{array} + \begin{array}{c}\text{Me}\\ \text{HOSiOH}\\ \text{Me}\end{array} \rightarrow \text{Siloxane oligomers}$$

It is known from earlier studies [12] that efficient unzipping may occur also in the presence of base.

3. Experimental details

3.1. Substrates

Decamethylpentasiloxane-1,5-diol (**3**), pentamethyldisiloxanol (**2**) and undecamethylpentasiloxane-1-ol (**4**) were synthesized and purified as described previously [10]. Tetramethyldisiloxane-1,3-diol (**1**) was obtained by hydrolysis of 1,3-dichlorotetramethyldisiloxane at −5°C in diethyl ether in the presence of 10 mol% excess of pyridine [10]; it was purified by recrystallization from a n-heptane-diethyl ether mixture; m.p. 65°C. Additional purification of **2** on a silica gel was necessary to remove traces of pyridine.

3.2. Solvent

Dioxane was purified by a standard method [26].

3.3. Catalyst

Trifluoromethanesulfonic acid (Fluka) was freshly distilled on a high vacuum line into a small thin-wall glass ampoule, which was placed in a side-arm of an ampoule containing solvent and crushed with a special hammer after evacuation of the ampoule on a high vacuum line. The solution of the acid was prepared in this way.

3.4. Kinetic studies

Reactions for kinetic studies were performed under purified nitrogen in a thermostated ampoule equipped with a Teflon stopcock. Solutions for the kinetic studies were prepared by use of high-precision Hamilton syringes. The time of the introduction of the catalyst to a thermostated solution of the substrate was taken as the zero time for the reaction. 50 μL samples were withdrawn at regular intervals with the Hamilton syringe and transferred to small ampoules containing a considerable excess of a catalyst-deactivating and trimethylsilylating agent. The time of the addition of the sample to the quenching solution was used to define the reaction time. In the case of the oligomers **3** and **4**, an aliquot of BSA (bistrimethylsilylacetamide) was used as the quenching and silylating agent, while in the case of substrate **1** three aliquots of a mixture of Et_3N and Me_3SiCl was used. The silylated samples were subjected to the GLC analysis. In the case of **2**, the reaction was quenched with an excess of pyridine; this allowed the disproportionation and condensation products to be distinguished.

3.5. GLC analysis

The analyses were performed with a Jeol JGC-1100 chromatograph with a thermal conductivity detector linked to a Takeda Riken 2215 A integrator; the conditions were: 2 m column, ∅ 3 mm, filled with 10% of OV-101 on Varaport 60/80 mesh, carrier gas hydrogen 40 mol min^{-1}; column temperature programmed 20–280°C, 15°C min^{-1}. Undecane or tridecane were usually used as internal standards. Retention times and molar response coefficients were determined separately with a standard mixture of the oligomers. A sample chromatogram is shown in Fig. 6.

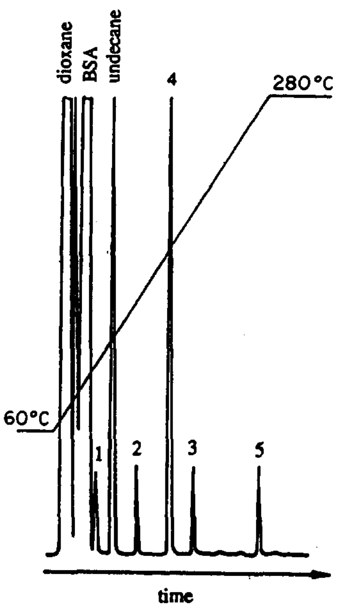


Fig. 6. Gas liquid chromatogram of the product mixture from $Me(Me_2SiO)_5H$, **4** in dioxane at 35°C in the presence of CF_3SO_3H; $[CF_3SO_3H]_0 = 2 \cdot 10^{-4}$ mol dm^{-3}, $[\mathbf{4}]_0 = 0.5$ mol dm^{-3}, $[H_2O]_0 = 1$ mol dm^{-3}, at 40% of the substrate conversion. The mixture was silylated with BSA. 1 – $(Me_2SiO)_4$ (a product of side reaction: $4 \xrightarrow{H^+} (Me_2SiO)_4 + Me_3SiOH$); 2 – $Me(Me_2SiO)_4SiMe_3$; 3 – $Me(Me_2SiO)_6SiMe_3$; 4 – $Me(Me_2SiO)_5SiMe_3$; 5 – $Me(Me_2SiO)_9SiMe_3$.

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