

# Acid-Catalyzed Condensation of Model Hydroxyl-Terminated Dimethylsiloxane Oligomers. Cyclization vs. Linear Condensation: Intra-Inter Catalysis

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**ABSTRACT:** Kinetics of the acid-catalyzed condensation of the model oligosiloxanols 1,1,3,3,5,5,7,7,9,9-decamethylpentasiloxane-1,9-diol (1), 1,1,3,3,5,5,7,7,9,9,9-undecamethylpentasiloxane-1-ol (2), and 1,1,3,3,3-pentamethylidisiloxane-1-ol (3) were studied in dioxane and in methylene chloride solutions. The reaction is accompanied by some processes involving siloxane bond cleavage. The condensation of 1 in dioxane shows classical kinetics of ring formation with competing linear growth, complying with the dilution rule of cyclization enhancement. In contrast, this rule does not work for the process in methylene chloride since cyclization in this solvent exhibits the same second-order kinetics in the substrate as the intermolecular condensation. This is explained by the base autocatalysis of the process with the substrate, which picks up a proton from the silanol group exerting nucleophilic attack. This catalysis is intramolecular for linear growth and intermolecular for cyclic product formation (intra-inter catalysis). In dioxane solution this autocatalysis is not observed since it is dominated by the assistance of the solvent molecule. This mechanism was confirmed by comparison of kinetic results of the condensation of reactants 1, 2, and 3 and by hydrogen bonding studies of these model oligomers.

## Introduction

Polycondensation involving silanol groups is one of the most important reactions in the synthesis of siloxane polymers and is commonly involved in the manufacturing of many silicone products.<sup>1-3</sup>

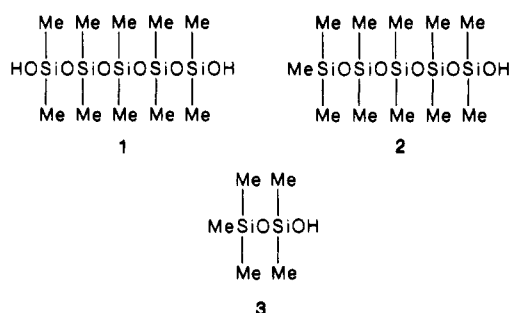
It also plays an important role in the mechanism of cationic polymerization of cyclic siloxanes.<sup>4-5</sup> For a long time the reaction has been the subject of intensive studies. Interesting results on the polycondensation of polymeric siloxanediols in emulsion were reported;<sup>6</sup> however, quantitative research in a homogeneous system was devoted mainly to monomeric models, triorganosilanol<sup>7-9</sup> and diorganosilanol<sup>10-17</sup>. The silanol group at the end of the polymer chain may show somewhat different behavior, since the chain including the other end group may actively participate in the reaction. In particular, the competition between intermolecular and intramolecular condensation, leading to cyclic products, has not yet been the subject of a deeper investigation. Polycondensation processes are also expected to be accompanied by processes involving siloxane bond cleavage.

It should also be mentioned that the kinetic studies of acid-catalyzed silanol condensation have been so far performed in solvents having proton acceptor properties like dioxane<sup>8-14</sup> or methanol,<sup>7,13-17</sup> which are able to function as bases in the reaction system. However, polycondensation in acid-base inert solvents such as methylene chloride, which may occur according to a different kinetic law, resembles more closely the process used in the synthesis of dimethylsiloxane polymers.

In such a solvent some reactive groups in the polymer, such as other silanol end groups and the polymer chain itself, i.e., siloxane units, may play a role, which in proton-accepting medium is performed by the solvent molecule (a preliminary paper<sup>18</sup>).

Association phenomena involving the silanol group (hydrogen bond) were found to play an important role in emulsion polycondensation of hydroxyl-terminated polysiloxanes.<sup>6</sup> They also were paid considerable attention in the cationic polymerization of cyclosiloxanes<sup>4,19,20</sup> and in the acid-catalyzed cleavage of the siloxane bond.<sup>5,21</sup> Elucidation of the possible interaction of terminal silanol groups with each other and of the siloxane chain atom with

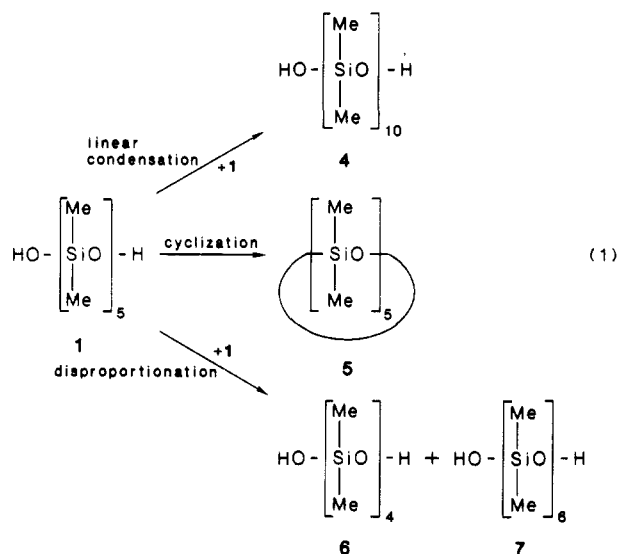
the terminal silanol group in the polysiloxanol condensation was the main purpose of this study. The problem was approached by kinetic investigations of the condensation of model siloxane oligomers 1, 2 and 3 having silanol end groups.



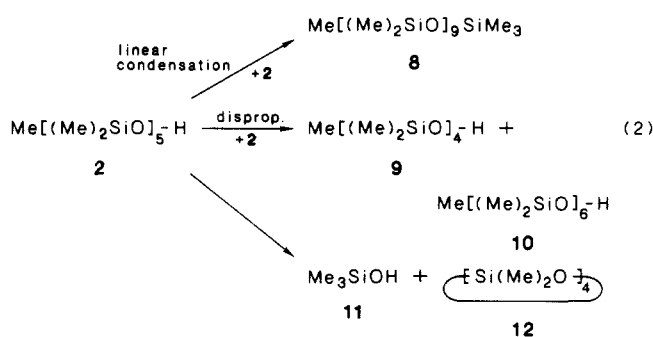
The condensation was performed in the presence of the protonic acids  $\text{CF}_3\text{SO}_3\text{H}$  and  $\text{CH}_3\text{SO}_3\text{H}$  in dioxane as a proton-accepting solvent and in methylene chloride as a nonintervening solvent. Since hydrogen bond (H-bond) interaction involving the substrate was one of the most important factors determining the kinetics, the research was supplemented with studies of this interaction in a solution of the model polysiloxanols in an inert solvent—carbon tetrachloride.

## Results and Discussion

**1. Principal Directions of the Reactivity of Hydroxyl-Ended Poly(dimethylsiloxane) Oligomers in the Presence of Acids.** The condensation of compounds 1, 2, and 3 was followed by gas-liquid chromatographic analysis. Gas chromatograms of the acid-catalyzed condensation system of the oligomer 1 taken at the beginning of the process (Figure 1) revealed products of competitive reactions: intermolecular condensation—eicosamethyldecasiloxane-1,19-diol (4)—and intramolecular condensation—decamethylcyclopentasiloxane (5). Two other linear polysiloxanediols also appeared, one having four and the other six siloxane units. The presence of these compounds in equimolar concentrations gave evidence that the condensation processes are accompanied by the disproportionation of the polysiloxanediols. Thus in its first stage, the process occurs according to reaction 1.



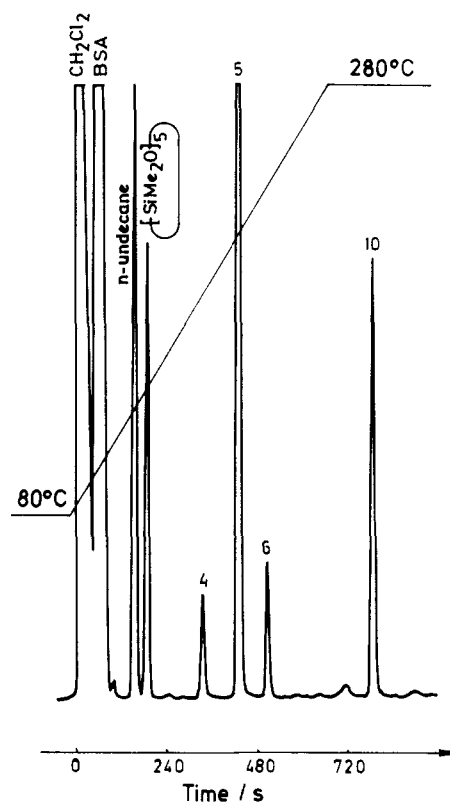
Products 4, 6, and 7 undergo further disproportionation and condensation, leading eventually to the formation of a full series of these oligohomologues. Oligomers 2 and 3 undergo a similar disproportionation. In addition, another cleavage process of 2 was observed, leading to the formation of trimethylsilanol (11) and octamethylcyclotetrasiloxane (12). The main reactions that take place in the beginning of the transformation of 2 are represented in reaction 2.



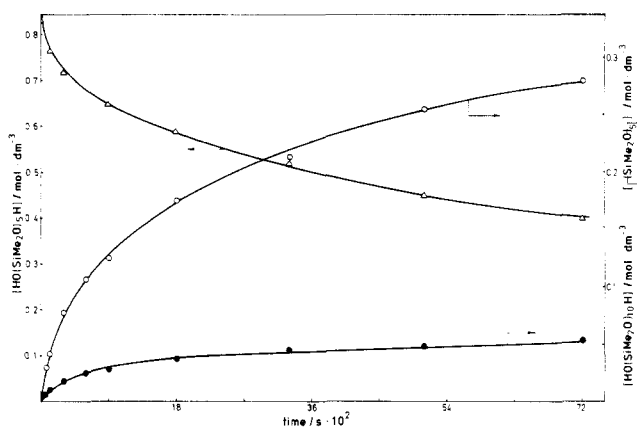
Contribution from reactions involving siloxane bond cleavage is strongly dependent on the conditions of the process, in particular, on the medium, catalyst, and concentrations. This paper is mainly devoted to the competition between the cyclization and the linear condensation, while the disproportionation will be discussed elsewhere.

**2. Condensation in Dioxane.** The kinetics of the condensation of compounds 1 and 2 in dioxane solution catalyzed with  $\text{CF}_3\text{SO}_3\text{H}$  and  $\text{CH}_3\text{SO}_3\text{H}$  were investigated. The conversion of the substrate and the formation of cyclic and linear products were followed by GLC up to at least 60% of the substrate conversion (Figure 2).

Serious complications are caused by water released in the course of the reaction. In the absence of water the reaction occurs selectively toward the condensation products; however, in the presence of small amounts of water, hydrolytic processes involving siloxane bond cleavage (reactions 1 and 2) are observed and their contribution seems to increase with the water content. Thus these side reactions become more important with substrate conversion. In addition, the presence of water strongly decreases the condensation rate catalyzed with  $\text{CF}_3\text{SO}_3\text{H}$ , because the activity of the strong acid is reduced.<sup>22-24</sup> Consequently, the condensation slows down distinctly as it proceeds (see Figure 2). In order to overcome these difficulties only the initial rate is taken into consideration in the kinetic analysis.



**Figure 1.** Gas chromatogram of the trimethylsilylated reaction mixture of  $\text{HO}[(\text{Me})_2\text{SiO}]_5\text{H}$  in  $\text{CH}_2\text{Cl}_2$  in the presence of  $\text{CH}_3\text{SO}_3\text{H}$  at  $35^\circ\text{C}$  taken at 30% of the substrate conversion. Initial concentrations of the substrate and the catalyst were  $0.20$  and  $1.00 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ , respectively. Unless denoted otherwise signals of trimethylsilylated linear oligomers  $\text{HO}[(\text{Me})_2\text{SiO}]_n\text{H}$  are denoted by  $n$ . Undecane is the internal standard and BSA is the silylating agent used in excess.



**Figure 2.** Substrate conversion-time and product formation-time dependences for the condensation of  $\text{HO}[(\text{Me})_2\text{SiO}]_5\text{H}$  in dioxane in the presence of  $1.00 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3} \text{ CF}_3\text{SO}_3\text{H}$  at  $35^\circ\text{C}$ : ( $\Delta$ )  $\text{HO}[(\text{Me})_2\text{SiO}]_5\text{H}$ ; ( $\circ$ )  $[(\text{Me})_2\text{SiO}]_5$ ; ( $\bullet$ )  $\text{HO}[(\text{Me})_2\text{SiO}]_{10}\text{H}$ .

The effect of water on the rate seems to be less important for the condensation with weaker methanesulfonic acid, which is also a less effective catalyst. In fact, the presence of a little water in dioxane increases the catalytic power of  $\text{CH}_3\text{SO}_3\text{H}$ . This phenomenon has been observed earlier<sup>22</sup> and attributed to the facilitation of the ionization of some protonic acid in nonpolar dioxane.

The series of runs at different initial acid and substrate concentrations permitted the determination of the kinetic law. Experiments were also performed with  $1 \text{ mol}\cdot\text{dm}^{-3}$  of water introduced initially to the system. Although water changed the rate and caused side reactions, it did not affect

Table I  
Results of Kinetic Studies of Oligosiloxanol Condensation in Dioxane Solution at 35 °C

substrate	concn range, mol·cm <sup>-3</sup>	cat.	concn range, mol·dm <sup>-3</sup>	[H <sub>2</sub> O] <sub>0</sub> , mol·dm <sup>-3</sup>	k <sub>L</sub> , mol <sup>-2</sup> ·dm <sup>6</sup> ·s <sup>-1</sup>	k <sub>c</sub> , mol <sup>-1</sup> ·dm <sup>3</sup> ·s <sup>-1</sup>	C <sub>eff</sub> = k <sub>c</sub> /k <sub>L</sub> , mol·dm <sup>-3</sup>
HO[Si(Me) <sub>2</sub> O] <sub>5</sub> H	0.1-1	CF <sub>3</sub> SO <sub>3</sub> H	(1-10) × 10 <sup>-4</sup>	0	0.69	8.0	11.6
	0.1-1		2 × 10 <sup>-4</sup>	1.0	0.0077	0.15	19.6
Me[Si(Me) <sub>2</sub> O] <sub>5</sub> H	0.1-1	CF <sub>3</sub> SO <sub>3</sub> H	2 × 10 <sup>-4</sup>	0	1.2		
	0.15-0.5		(2-40) × 10 <sup>-4</sup>	1.0	0.0062		
Me[Si(Me) <sub>2</sub> O] <sub>5</sub> H	0.5	CH <sub>3</sub> SO <sub>3</sub> H	5 × 10 <sup>-3</sup>	0	2.5 × 10 <sup>-4</sup>		
	0.5		5 × 10 <sup>-3</sup>	1.0	1.09 × 10 <sup>-3</sup>		

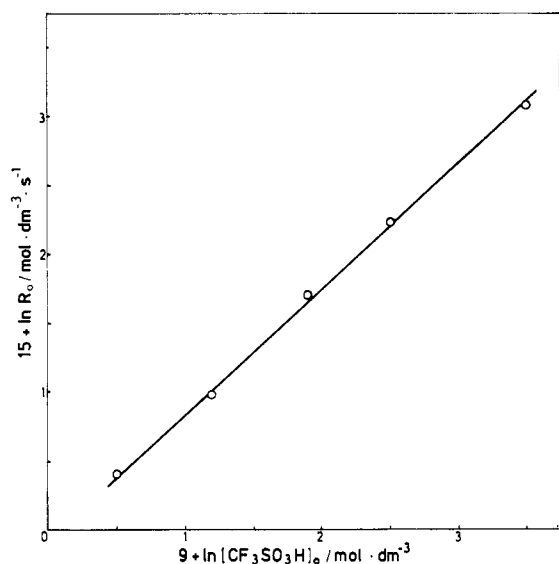
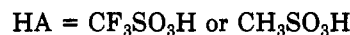


Figure 3. Dependence of the initial rate of Me[(Me)<sub>2</sub>SiO]<sub>9</sub>SiMe<sub>3</sub> formation  $R_0$  in the polycondensation of 0.50 mol·dm<sup>-3</sup> Me[(Me)<sub>2</sub>SiO]<sub>5</sub>H on the catalyst concentration. Solvent dioxane with [H<sub>2</sub>O]<sub>0</sub> = 1.0 mol·dm<sup>-3</sup>; 35 °C.

the general shape of the kinetic law, which is represented by (Figures 3 and 4)

(a) ring formation

$$\left(\frac{d[5]}{dt}\right)_{t=0} = k_c[HA][1]$$



(b) linear oligomer formation

$$\left(\frac{d[X]}{dt}\right)_{t=0} = qk_L[HA][Y]^2 \quad (I)$$

where substrate Y is oligomer 1 or 2, product X is oligomer 4 or 8, and the statistical factor  $q$  is 4 and 1 for reactants 1 and 2, respectively.

As expected, the unimolecular cyclization is first order with respect to substrate 1, while the bimolecular chain coupling is second order in 1 and in 2. The condensation of 1 in dioxane thus shows a classical competition between intramolecular and intermolecular condensation. Dilution of the system retards strongly the intermolecular condensation, increasing the yield of the cyclic product. The effective concentration of the SiOH group for which the rate of the intermolecular and intramolecular reactions regarding the statistical factor are equal<sup>25,26</sup> can be deduced from the intersection point of the kinetic lines for the cyclization and the chain coupling in the double-logarithmic plot of specific rate vs. initial concentration (Figure 4). As seen in Table I, where the kinetic data in dioxane are summarized, the effective concentration  $C_{eff}$  adopts a very high value, reflecting a strong ring formation tendency in this system.

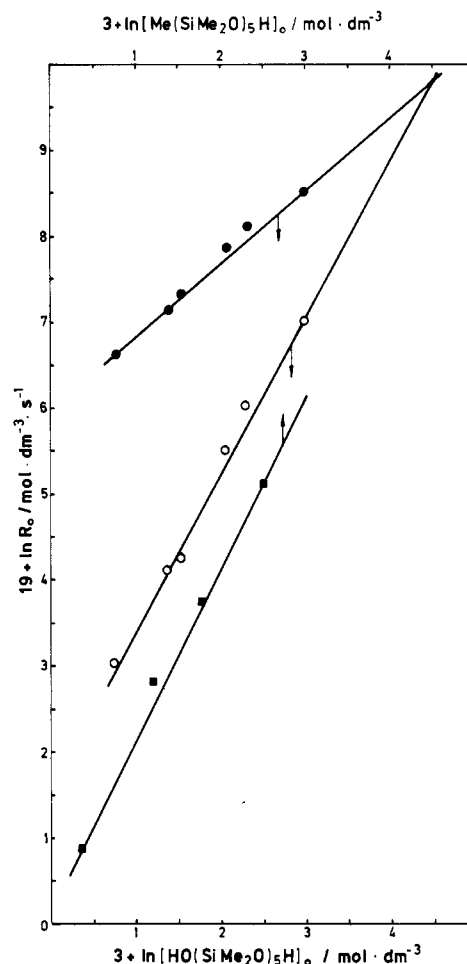
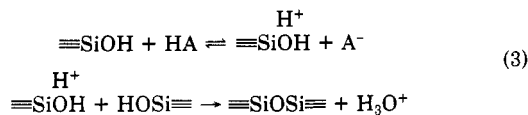


Figure 4. Dependence of initial rates of product formation  $R_0$  on the initial substrate concentration in the condensation of HO[(Me)<sub>2</sub>SiO]<sub>5</sub>H and Me[(Me)<sub>2</sub>SiO]<sub>5</sub>H in dioxane with [H<sub>2</sub>O]<sub>0</sub> = 1.0 mol·dm<sup>-3</sup> at 35 °C in the presence of 2.0 × 10<sup>-4</sup> mol·dm<sup>-3</sup> CF<sub>3</sub>SO<sub>3</sub>H. The formation of (●) [(Me)<sub>2</sub>SiO]<sub>6</sub>; (○) HO[(Me)<sub>2</sub>SiO]<sub>10</sub>H; (■) Me[(Me)<sub>2</sub>SiO]<sub>9</sub>SiMe<sub>3</sub>.

In order to check the effect of the OH group at the other chain end of oligomer 1 on the reactivity in the bimolecular condensation, the initial specific rates of the condensations of 1 and 2 were compared. Nearly the same values of the rate constants for both reactants were observed in the system having initial water, although in the absence of initial water the reaction of 2 was a little faster. The difference could be attributed to a higher concentration of H<sub>2</sub>O produced in the condensation of 1 due to an intensive cyclization reaction. These results do not seem to indicate any larger specific effect of the remaining SiOH group. If some effect exists, it is directed toward the decrease of the reactivity.

The kinetic law is in agreement with a classical mechanism of acid-catalyzed silanol condensation according to reaction 3, which has been proposed to operate in dioxane by Lasocki and Chrzczonowicz<sup>13</sup>



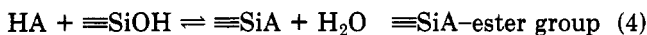
**3. Studies of the Polysiloxanol Condensation in Methylene Chloride.** **3.1. Kinetic Law.** Polycondensation proceeds much faster in methylene chloride than in dioxane under the same conditions because the acid shows a higher activity in the acid-base inert solvent. The condensation of 1 catalyzed with  $\text{CF}_3\text{SO}_3\text{H}$  was too fast to be conveniently followed by a routine sampling technique, half-life times were in the range 1–20 s. The kinetic studies were limited to the process with methanesulfonic acid as the catalyst, for which the half-life times were of the order of 0.5–5 h. Kinetic law was different and more complicated than that for the condensation in dioxane. The addition of small amounts of water increases the rate as shown in Figure 5. The effect of water is also manifested in the peculiar shape of the kinetic curves (Figure 6), which approach straight lines in a zero-order kinetic coordinate system. Such kinetics are characteristic for processes autocatalyzed by a product, and water released in the course of the condensation is responsible for this autocatalytic effect.

To a first approximation, the initial rate was correlated with concentrations using uninomial eq II analogous to those found for the reaction in dioxane.

$$\begin{aligned} \left(\frac{d[5]}{dt}\right)_{t=0} &= k_c[\text{HA}]^m[\text{1}]^n \\ \left(\frac{d[\text{X}]}{dt}\right)_{t=0} &= qk_L[\text{HA}]^m[\text{Y}]^n \quad (\text{II}) \end{aligned}$$

where Y is 1, 2, and 3 and X is the respective linear product.

The correlation is presented in Figures 7 and 8 and the corresponding values of the  $m$  and  $n$  exponents are given in Table II. The fractional values of the  $n$  exponent can be explained by taking into account the esterification of the silanol group (reaction 4). Since this process proceeds

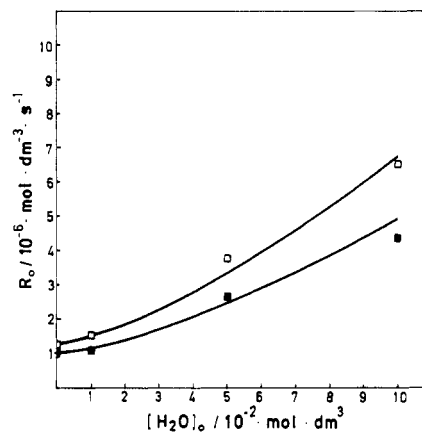


with the rate at least one order of magnitude higher than the condensation<sup>5,20</sup> and since the concentration of the acid is small, equilibrium 4 determines stationary acid and ester concentrations.

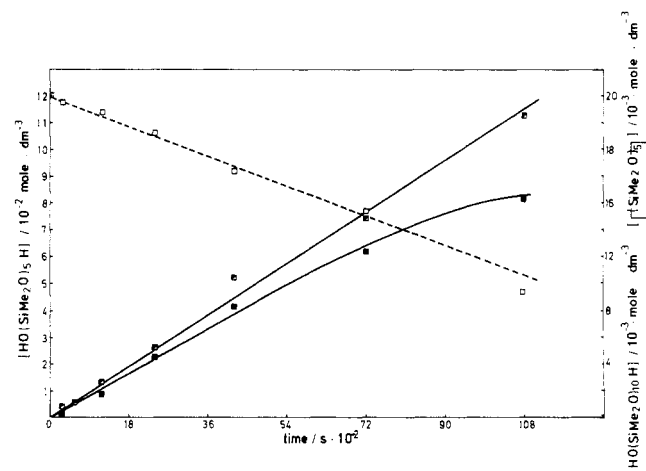
Equilibrium 4 in dioxane lies well to the acid side, which is stabilized by strong hydrogen bonding to the solvent molecules. However, in solvents like methylene chloride, which is unable to stabilize the acid by the H-bond interaction, a considerable portion of the catalyst is transformed into the ester. This behavior may have serious mechanistic consequences, since in addition to the classical scheme of the condensation operating in dioxane, the process may involve a cross-condensation according to reaction 5.



Computer simulations of the kinetics of the condensation of 1, 2, and 3 were performed by taking into account equilibrium 4 and equilibrium of the H-bond formation of the acid with the substrate (see Experimental Section). With the assumption of some reasonable values of the equilibrium constants, it was shown that a good correlation could be obtained according to eq III (see also Figure 13). When complications which will be discussed in second 3.2



**Figure 5.** Effect of water initially introduced into the system on rates of product formation in the condensation of  $0.10 \text{ mol} \cdot \text{dm}^{-3}$   $\text{HO}[(\text{Me})_2\text{SiO}]_5\text{H}$  in methylene chloride with  $1.00 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$   $\text{CH}_3\text{SO}_3\text{H}$  at  $35^\circ\text{C}$ : (□)  $[(\text{Me})_2\text{SiO}]_5$ ; (■)  $\text{HO}[(\text{Me})_2\text{SiO}]_{10}\text{H}$ .



**Figure 6.** Substrate conversion-time and product formation-time curves for the condensation of  $\text{HO}[(\text{Me})_2\text{SiO}]_5\text{H}$  in methylene chloride with  $1.00 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$   $\text{CH}_3\text{SO}_3\text{H}$  at  $35^\circ\text{C}$ : (□)  $\text{HO}[(\text{Me})_2\text{SiO}]_5\text{H}$ ; (■)  $[(\text{Me})_2\text{SiO}]_5$ ; (●)  $\text{HO}[(\text{Me})_2\text{SiO}]_{10}\text{H}$ .

are taken into account, these equations are well interpreted in terms of the simple SiOH group condensation analogous to that shown in reaction 3.

$$\begin{aligned} \text{(a) cyclization} \quad & \frac{d[5]}{dt} = k_c'[\text{HA}]_f[\text{1}]^2 \\ \text{(b) linear condensation} \quad & \frac{d[\text{X}]}{dt} = qk_L'[\text{HA}]_f[\text{Y}]^{n'} \quad (\text{III}) \end{aligned}$$

where Y and X are defined in eq II and  $[\text{HA}]_f$  is the stationary concentration of free (H-bond uncomplexed) acid. The corresponding values of  $n'$  are given in Table II.

It was also found that the kinetic data could be equally well interpreted in terms of eq IV (Table VI), corresponding to the cross-condensation mechanism under the assumption that one water molecule participates in the condensation.

$$\begin{aligned} \frac{d[5]}{dt} &= k_c''[\text{H}_2\text{O}][\text{SiA}]_{st}[\text{1}] \\ \frac{d[\text{X}]}{dt} &= k_L''[\text{H}_2\text{O}][\text{SiA}]_{st}[\text{Y}]^{n'-1} \quad (\text{IV}) \end{aligned}$$

$[\text{SiA}]_{st}$  is the stationary concentration of the ester.

Table II  
Comparison of Rates and Kinetic Parameters for the Condensation of Polysiloxanols in  $\text{CH}_2\text{Cl}_2$  at 35 °C in the Presence of  $1.0 \times 10^{-4} \text{ mol dm}^{-3} [\text{CH}_3\text{SO}_3\text{H}]$

substrate	condensation type	product formation rate at $[\text{C}]_0 = 0.02 \text{ mol} \cdot \text{dm}^{-3}$ , $\text{mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$	rel linear product formation rate (with statistical factor)	apparent order		fitted order <sup>a</sup>	
				in cat. $m$	in substrate $n$	in cat. $m'$	in substrate $n'$
$\text{HO}[\text{Si}(\text{Me})_2\text{O}]_5\text{H}$	linear	$1.7 \times 10^{-7}$	1	1.0	1.4	1	2
	ring formation	$1.7 \times 10^{-7}$		1.0	1.4	1	2
$\text{Me}[\text{Si}(\text{Me})_2\text{O}]_5\text{H}$	linear	$1.26 \times 10^{-9}$	0.030	1.0	1.7	1	2
$\text{Me}_3\text{SiOSi}(\text{Me})_2\text{OH}$	linear	$0.89 \times 10^{-10}$	0.0021	1.0	2.6	1	3

<sup>a</sup>The order resulting from the simulation procedure (see Experimental Section).

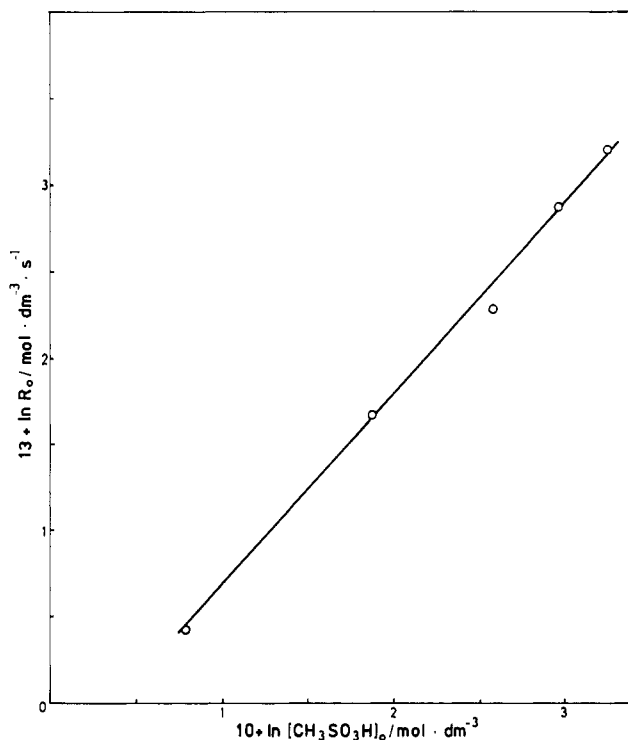
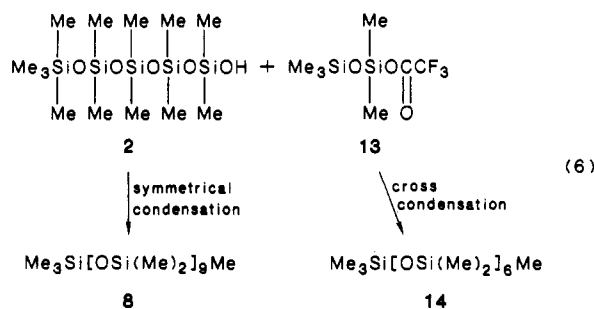


Figure 7. Dependence of the initial rate of substrate consumption  $R_0$  on catalyst concentration in the condensation of  $0.10 \text{ mol} \cdot \text{dm}^{-3} \text{HO}[(\text{Me})_2\text{SiO}]_5\text{H}$  in methylene chloride at 35 °C.

Both mechanisms are, therefore, indistinguishable on the basis of kinetic law.

In an attempt to clarify this problem we performed a cross-experiment according to reaction 6



Unfortunately, this test could not be done for the highly unstable esters of  $\text{CF}_3\text{SO}_3\text{H}$  and  $\text{CH}_3\text{SO}_3\text{H}$ , which had to be replaced by the less reactive ester trifluoroacetic acid. The evaluation of the relative rates of formation of 8 and 14 was done only for the initial phase of the process, to eliminate possible perturbation from the end-group exchange between the reactants. Under the conditions used (initial concentrations,  $[\text{2}] = 0.35 \text{ mol} \cdot \text{dm}^{-3}$ ,  $[\text{13}] = 0.35 \text{ mol} \cdot \text{dm}^{-3}$ ; temperature, 35 °C), products from both reac-

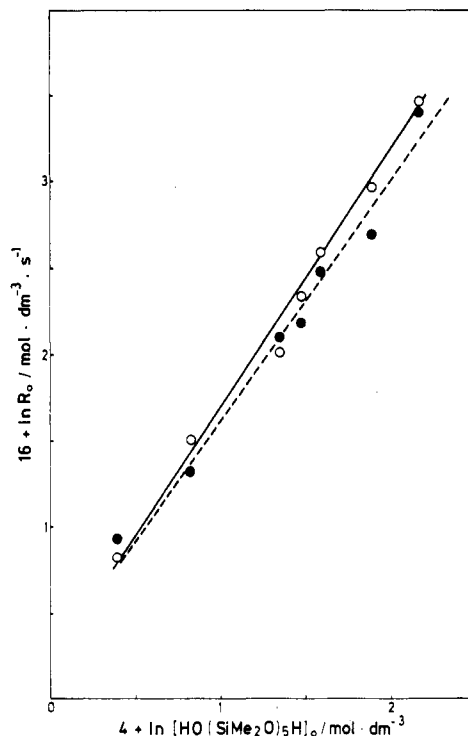


Figure 8. Dependence of the initial rate of the ring formation (—) and the intermolecular condensation (---) on the initial substrate concentration in the condensation of  $\text{HO}[(\text{Me})_2\text{SiO}]_5\text{H}$  in methylene chloride with  $1.00 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3} \text{CH}_3\text{SO}_3\text{H}$ .

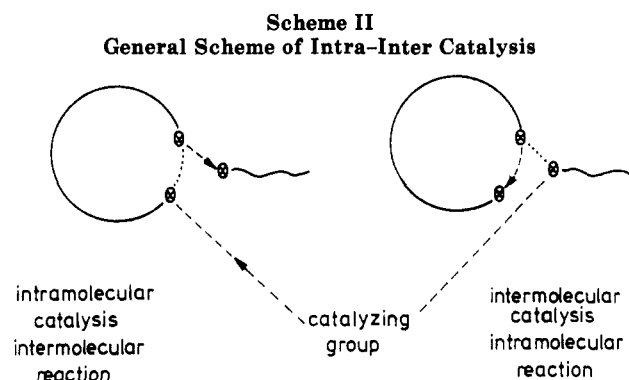
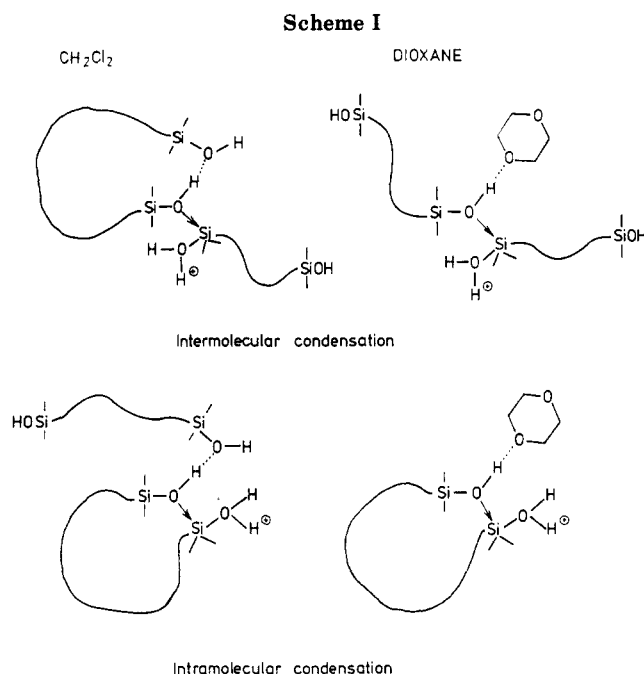
tions appeared. When the statistical factor of 2 was corrected for, the symmetrical condensation proved to be faster than the cross-condensation by a factor of 3.3. Thus the general conclusion from the cross-experiment is that both types of condensation may occur and that the experimental conditions and the structure of the end groups decide which is the dominating process. Assuming that the behavior of methanesulfonic acid ester is similar and taking into account that the stationary ester concentration in the condensation system is much lower than the initial ester concentration in the cross-experiment, we believe that the classical mechanism of the condensation dominates here. On the other hand, the cross-condensation is perhaps more important in the cationic polymerization of cyclic siloxanes, where the stationary concentration of the ester is higher than the stationary concentration of the silanol group.<sup>5,19</sup>

**3.2. Unusual Competition of Linear Condensation and Cyclization.** The data presented in Figure 8 and Table II permit a comparison of the kinetics of ring formation and linear growth in methylene chloride. The mechanisms of these processes on the level of end-group reaction should be the same since the end groups in substrate 1 are separated by a chain long enough to react

**Table III**  
**Effect of Dilution on the Yield of Cyclic Oligomers in the Polycondensation of HO[Si(Me)<sub>2</sub>O]<sub>5</sub>H (1) in Methylene Chloride Catalyzed with Methanesulfonic Acid at 35 °C for a 65% Monomer Conversion [CH<sub>3</sub>SO<sub>3</sub>H]<sub>0</sub> = 5.0 × 10<sup>-4</sup>**

[HO(SiMe <sub>2</sub> O) <sub>5</sub> H] <sub>0</sub> , mol·dm <sup>-3</sup>	yield of cyclics, mol/(mol converted 1)					
	(SiMe <sub>2</sub> O) <sub>5</sub>		(SiMe <sub>2</sub> O) <sub>10</sub>		(SiMe <sub>2</sub> O) <sub>15</sub>	
	obsd	theor <sup>a</sup>	obsd	theor <sup>a</sup>	obsd	theor <sup>a</sup>
2.0 × 10 <sup>-1</sup>	0.25		2.1 × 10 <sup>-3</sup>		6 × 10 <sup>-4</sup>	
2.0 × 10 <sup>-2</sup>	0.30	0.77	2.4 × 10 <sup>-3</sup>	2.1 × 10 <sup>-2</sup>	1.5 × 10 <sup>-3</sup>	6 × 10 <sup>-3</sup>

<sup>a</sup>The yield expected from the dilution rule.



independently and the 10-membered siloxane ring formed is strainless.<sup>27</sup> Some differences in kinetic law are expected due to the differences in the molecularity of these condensation reactions. It was surprising to observe that the apparent order with respect to the substrate and the order resulting from the simulation are the same for the unimolecular cyclization and for the bimolecular linear growth of oligomer 1. The dilution of the system does not change the relation of the yield of cyclic and linear products. In full contrast to the condensation in dioxane, even at a very low concentration of 1, in methylene chloride the yield of the linear product remains high.

This phenomenon is more general since the mole ratio of the cyclic to the linear product is independent of the substrate concentration even when trifluoroacetic acid or trifluoromethanesulfonic acid is used as the catalyst. In the case of the catalysis with CH<sub>3</sub>SO<sub>3</sub>H the ratio remains at the level close to 1:1 with dilution, while for CF<sub>3</sub>COOH and CF<sub>3</sub>SO<sub>3</sub>H the respective values were 1:0.75 and 1:1.4.

Yields of higher cyclics in the polycondensation system, i.e., the cyclic dimer and trimer of 1, are increasing slightly with the dilution but much less than expected from the classical competition kinetic law (Table III).

The explanation of this phenomenon must invoke the participation of another substrate molecule in the cyclization process. The role of this molecule must be specific for methylene chloride solvent because in dioxane the usual first-order kinetics of the cyclization was observed. However, this additional substrate molecule does not intervene in the intermolecular reaction of 1 showing a classical second-order kinetics for the catalyzed bimolecular process.

The concept is presented in Scheme I. The condensation process must involve the proton abstraction from the attacking silicon OH group, thus it requires interaction

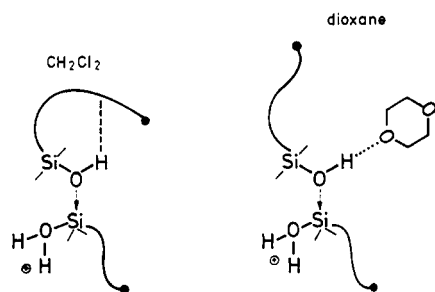
with a base. Two possible variants could be considered. In the first the proton removal occurs together with silicon-oxygen bond formation in one concerted and rate-limiting step. This is the case of general base catalysis. The other possibility is proton transfer in a step following the rate-limiting step. In this case the positive charge appears in the transition state on the hydrogen atom close to the reaction center. This charge requires stabilization by interaction with the base. Thus, in either case the hydrogen bond preassociation involving the proton under consideration is required. The function of the base in dioxane is performed by the solvent molecule able to interact with the acid (Scheme I).

In methylene chloride, however, this basic assistance may be rendered only by the substrate itself. The comparison of IR spectra of various silanol and siloxanes H-bond complexes drove West et al.<sup>28,29</sup> to the conclusion that the silanol group was a stronger proton acceptor than siloxane. Therefore, it is feasible to assume that it renders the basic assistance more readily. Ring formation condensation occurs with the participation of the silanol group from the other oligomer molecule, while the group at the other end of the chain gives assistance to intermolecular condensation (Scheme II). Thus, in both these cases two oligomer molecules participate in the formation of the transition state. We have here the competition of the intermolecular reaction intramolecularly catalyzed with the intramolecular reaction involving intermolecular catalysis. This phenomenon we call intra-inter catalysis.

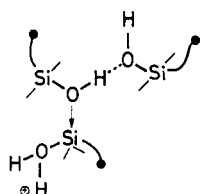
Further evidence for this mechanism comes from the comparison of the kinetics of the linear condensation of 1 with the condensation of oligomers 2 and 3 (Table II). The analogue of 1 having only one silanol end group—oligomer 2—undergoes the condensation in dioxane at a rate comparable to that of the linear condensation of 1 in this solvent. However, in methylene chloride the reactivity of 2 is distinctly smaller as compared with 1, giving further evidence that the silanol group at the other chain end plays a specific role in the linear condensation process.

If the basic assistance to the attacking silanol group remains important in the condensation of 2, then the apparent order with respect to the substrate is expected to be one unit higher for the reaction of 2 than for the respective reaction of 1, reflecting the participation of three

Scheme III

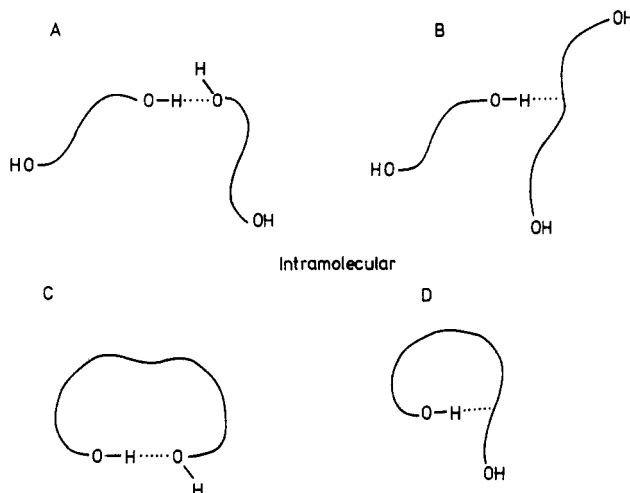


Scheme IV



Scheme V

Intermolecular



siloxanol molecules in the transition state. However, the apparent order of **2** is only slightly higher than that of the linear condensation of **1** and the data fit rather well to the equation of the second order with respect to the oligomer in the kinetic simulation procedure (Tables II and VI). The explanation invokes the basic assistance of the siloxane chain (Scheme III). If there is no silanol group at the other end of the chain then the intramolecular catalysis by a weaker base (siloxane group) determines the kinetic pattern.

Studies of hydrogen bonds (next paragraph) showed that such an assistance of the siloxane group is not likely to operate in the condensation of compound **3**. Consequently, from **2** to **3**, a one unit increase of the order in the substrate and a further drop in the reaction rate were observed (Table II), which reflects thermolecularity of the process due to intermolecular base catalysis by the substrate (Scheme IV).

These observations gave strong support to Scheme II expressing the concept of intra-inter catalysis determining the cyclization vs. linear growth competition. Certainly, this mechanism is limited to some region of the substrate concentration. The yield of the cyclic product in the polycondensation of **1** catalyzed with  $\text{CF}_3\text{SO}_3\text{H}$  was found to be more or less constant with the dilution of the system up to about  $10^{-2} \text{ mol}\cdot\text{dm}^{-3}$ .<sup>18</sup> However, with further dilution a distinct increase of the cyclic yield was observed, indicating the operation of another mechanism conforming to the dilution rule.

**4. Studies of the Hydrogen Bond Interaction of Siloxanol Oligomers.** Since we made a crucial point of H-bond preassociation in the interpretation of the strange cyclization kinetics, we hoped that study of this interaction in solutions of compounds **1**, **2**, and **3** in an inert solvent would permit the verification of our concept. It requires the domination of the silanol-silanol interaction over the silanol-siloxane one and the importance of the intramolecular complexation. The hydrogen bonds of **1**, **2**, **3** and trimethylsilanol (**13**) were studied in their solutions in carbon tetrachloride by IR spectroscopy in the region of the OH stretching vibration band ( $3000\text{--}3800 \text{ cm}^{-1}$ ). Methylene chloride could not be used here as the solvent because of its considerable absorbance in this region. The H-bond association pattern is expected to be analogous in  $\text{CCl}_4$  and  $\text{CH}_2\text{Cl}_2$ . In particular, the competition of the formation of intramolecular and intermolecular H bonds should be similar. The difference is that populations of respective associates in  $\text{CH}_2\text{Cl}_2$  are reduced as compared

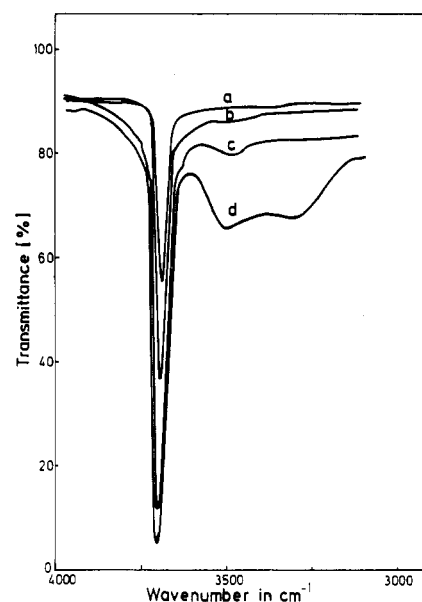


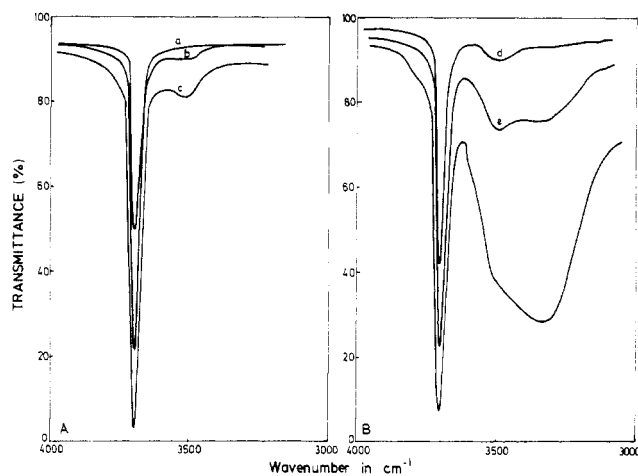
Figure 9. IR spectra of  $\text{Me}_3\text{SiOH}$  in  $\text{CCl}_4$  at  $35^\circ\text{C}$ . Concentrations in  $\text{mol}\cdot\text{dm}^{-3}$  are (a) 0.0080; (b) 0.0200; (c) 0.050; (d) 0.100. Path length, 2 mm.

with those in  $\text{CCl}_4$  solutions under the same conditions. Methylene chloride interacts more strongly with proton donors than  $\text{CCl}_4$ , which leads to the lower values of respective complex formation constants concerning solute-solute interactions.<sup>30</sup>

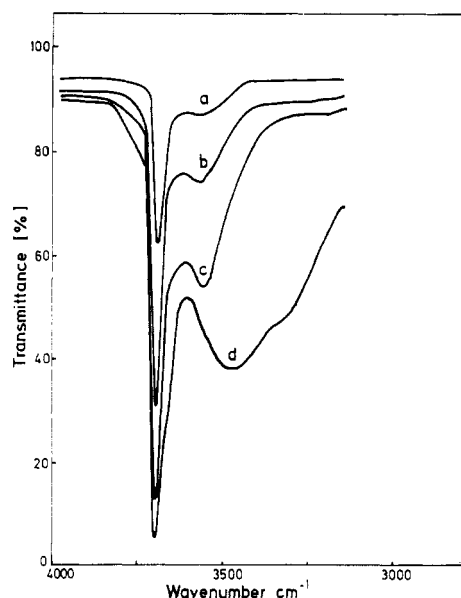
Four types of bimolecular complexes were considered: two silanol-silanol ones, the intermolecular (A) and the intramolecular (C), and two respective silanol-siloxane interactions (B) and (D) (Scheme V).

Silanol having free acidic OH function shows a sharp band at about  $3700 \text{ cm}^{-1}$ , while H-bonded silanol gives rise to a broad band at lower wavenumbers (Figures 9-12). The H-bonds of simple triorganosilanols and diorganosilanedols have been extensively studied.<sup>28,29,31-37</sup>

Some research on oligosiloxanols was done as well.<sup>38,39</sup> However, the comparison of spectra of **1**, **2**, **3**, and **11** taken at variable concentrations permits a deeper insight into the nature of the H-bond self-association in the poly(dimethylsiloxanol) system and more information pertinent to the problems considered in this research could be obtained. Inspection of the spectra leads to the conclusion that  $\text{SiOH}$  binary intermolecular homocomplex A gives rise



**Figure 10.** IR spectra of  $\text{Me}[(\text{Me})_2\text{SiO}]_2\text{H}$  in  $\text{CCl}_4$  at  $35^\circ\text{C}$ . Concentrations in  $\text{mol}\cdot\text{dm}^{-3}$  are (a) 0.0080; (b) 0.0200; (c) 0.040; (d) 0.100; (e) 0.200; (f) 0.50. Path length for A, 2 mm, for B, 0.25 mm.

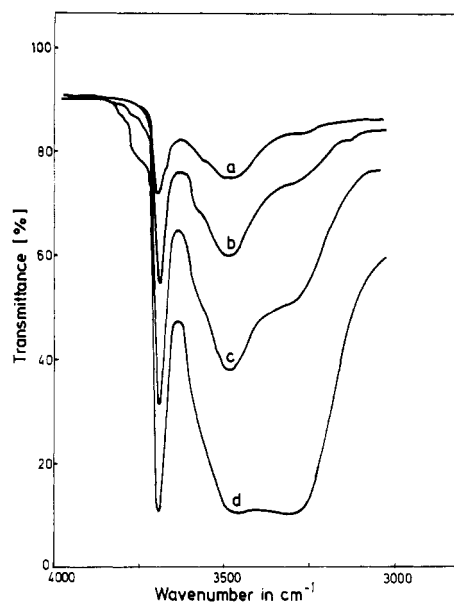


**Figure 11.** IR spectra of  $\text{Me}[(\text{Me})_2\text{SiO}]_5\text{H}$  in  $\text{CCl}_4$  at  $35^\circ\text{C}$ . Concentrations in  $\text{mol}\cdot\text{dm}^{-3}$  are (a) 0.0080; (b) 0.020; (c) 0.050; (d) 0.50. Path length for a, b, and c is 2 mm, for d is 0.25 mm.

to a band having a maximum about  $3500\text{ cm}^{-1}$  ( $\Delta\nu \sim 200\text{ cm}^{-1}$ ), which coincides with the band due to the intramolecular interaction of this type and may be easily overlooked (like in ref 38 and 39). Instead, the intensive broad band centered at about  $3300\text{ cm}^{-1}$  ( $\Delta\nu \sim 400\text{ cm}^{-1}$ ), which appears at higher concentrations, originates from the absorption by complexes comprising more than two silanol groups (polymeric H-bond complexes), which may be of linear or cyclic structure. Similar features in this wavenumber region were exhibited in the spectra of some alcohols (see for example ref 40 and 41) and simple silanols.<sup>28</sup>

The intramolecular silanol-siloxane heterocomplexes of **3** do not appear, as can be seen from the spectrum taken at the concentration low enough to neglect the intermolecular complexes (Figure 10A). This H-bond is formed readily in the case of model **2**, giving rise to absorption with the maximum shifted about  $130\text{ cm}^{-1}$  down from the free OH band.

This absorption also overlaps with the absorption from intermolecular bonding of this type shifted  $100\text{--}120\text{ cm}^{-1}$  from the free OH band. A lower wavenumber shift for these heterocomplexes than for the corresponding silanol homocomplex reflects a much weaker proton-accepting



**Figure 12.** IR spectra of  $\text{HO}[(\text{Me})_2\text{SiO}]_5\text{H}$  in  $\text{CCl}_4$  at  $35^\circ\text{C}$ . Concentrations of SiOH group in  $\text{mol}\cdot\text{dm}^{-3}$  are (a) 0.0080; (b) 0.0200; (c) 0.040; (d) 0.100. Path length, 2 mm.

**Table IV**  
Formation Constant  $K_A$  of OH Homocomplexes of  $\text{Me}_3\text{SiOSi}(\text{Me})_2\text{OH}$  (**3**) Calculated from Eq VII and  $K_A'$  Calculated from Eq VI on the Assumption That No Polymer Complexes Exist in the System  $\text{CCl}_4$  at  $35^\circ\text{C}$

$[\text{Me}_3\text{SiOSi}(\text{Me})_2\text{OH}]_0$ , $\text{mol}\cdot\text{dm}^{-3}$	$K_A'$ , $\text{mol}^{-1}\cdot\text{dm}^3$	$K_A$ , $\text{mol}^{-1}\cdot\text{dm}^3$
0.07	2.89	2.19
0.10	2.56	1.92
0.15	3.25	2.06
0.20	3.14	2.04
0.25	7.79	2.54
0.30	9.02	2.43
0.35	18.29	2.87
0.40	21.63	2.76

av  $2.3 \pm 0.5$

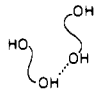
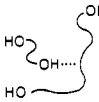
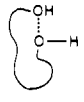
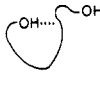
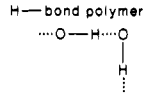
ability of siloxane oxygen as compared with silanol.

Approximate values of the formation constant for some H-bonded complexes were determined in a series of experiments at different concentrations measuring  $A_f$ , the absorbance at the maximum of the OH band of free silanol. The molar coefficient for this absorbance  $\epsilon_f$  was assumed to adopt the same value for **1**, **2**, and **3**. The constant  $K_B$  for the formation of the intermolecular complex **B** was approximated by studying the interaction of **3** with octamethylcyclotetrasiloxane (**12**) and assuming that the proton-accepting ability in the H-bond is the same for a siloxane bond in an unstrained ring of **12** and in a linear dimethylsiloxane chain of **1** and **2**. The constant  $K_A$  for the intermolecular homocomplex of the silanol group (**A**) was found from the spectra of **3** by taking into account complex **B**, which is also formed in this system.

Some additional assumptions concerning the multiplicity of complexes has to be done. One possible approach is the assumption that only binary complexes are formed, i.e., the silanol group bound in a complex as a proton donor cannot at the same time be bonded as a proton acceptor and vice versa. Results obtained under this assumption for  $K_A$ , ( $K_A'$ ) calculated from eq VI are shown in the second column of Table IV. Inspection of the data leads to the conclusion that the assumption is not justified even in relatively low concentrations. Thus, determination of  $K_A$  and  $K_B$  for single H-bonds was done with eq V and VII on the assumption that the engagement of the silanol

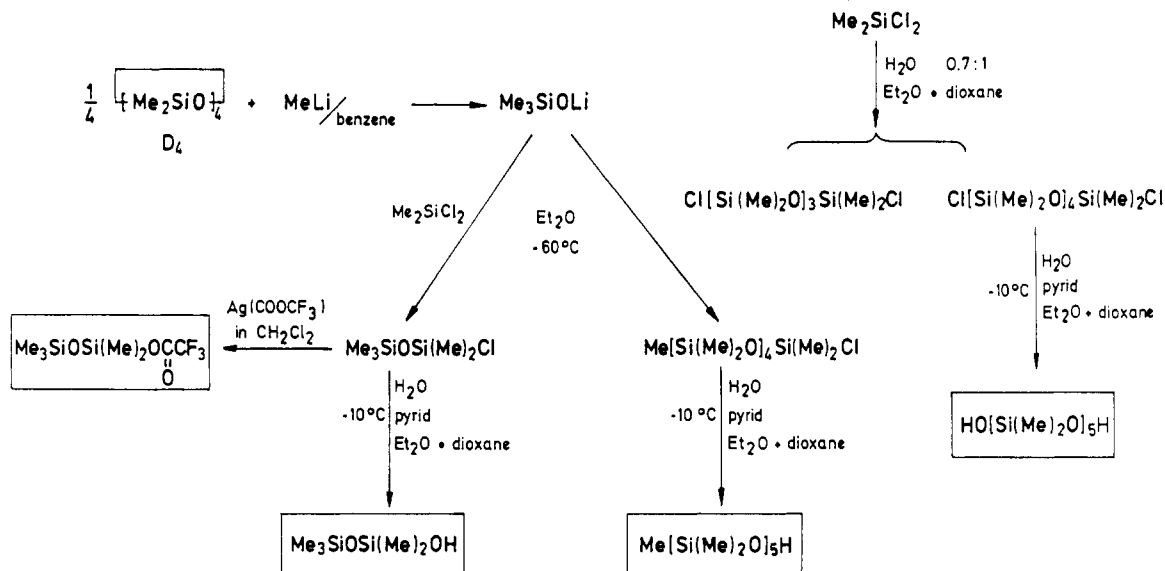


Table V  
Properties of Hydrogen Bond Complexes of HO[Si(Me)<sub>2</sub>O]<sub>5</sub>H

					
$\Delta\nu, \text{cm}^{-1}$	190	100	200	130	400
$K (35^\circ\text{C})$	$2.3 \text{ dm}^3 \cdot \text{mol}^{-1}$	$0.84 \text{ dm}^3 \cdot \text{mol}^{-1}$	$>2$	0.38	
$C_{\text{eff}}, \text{mol} \cdot \text{dm}^{-3}$		$0.21 \text{ dm}^3 \cdot \text{mol}^{-1 a}$	$>1$	0.45	

<sup>a</sup> Related to one siloxane bond.

Scheme VI



group in the multimolecular complex has no effect on the strength of the single H-bond.

$$K_B = \frac{[3]\epsilon_f L - A_f}{4A_f[12]} \quad (L \text{ is path length}) \quad (\text{V})$$

$$K_A' = \frac{[3] - \frac{A_f}{\epsilon_f L} (1 + K_B[3])}{\left\{ \frac{A_f}{\epsilon_f L} - \left( [3] - \frac{A_f}{\epsilon_f L} (1 + K_B[3]) \right) \right\}^2} \quad (\text{VI})$$

$$K_A = \frac{[3]\epsilon_f L - A_f(1 + K_B[3])\epsilon_f L}{A_f^2} \quad (\text{VII})$$

The results in column 3 of Table IV show that this assumption is only a crude approximation, since the  $K_A$  value tends to increase, indicating that engagement in a multiple complex makes the single interaction stronger. This behavior is in agreement with a higher wavenumber shift for the polymeric complexes.

The formation constant  $K_D$  for the intramolecular complex D was estimated from spectra of **2** (eq VIII) taken at concentrations low enough to avoid significant concentrations of complexes A and B.

$$K_D = [2] \frac{\epsilon_f L}{A_f} - 1 \quad (\text{VIII})$$

The application of the analogous procedure to estimate the formation constant  $K_C$  for complexes C from spectra of **1** proved to be impossible since  $K_C$  is much larger than  $K_D$  and the portion of OH group engaged in a strong

multiple H-bond interaction becomes significant even at a very low concentration of **1**.

Although the results are only an approximation, nevertheless they permit some general conclusions supporting the concept of the intra-inter catalysis to be drawn. They show a considerable tendency for the formation of ring H-bonded structures involving both silanol-silanol and silanol-siloxane complexations and point to a domination of the silanol-silanol interaction. They also show that there is a considerable tendency for the formation of multiple H-bond complexes, which means that the single H-bond increases to a large extent the acid-base strength of the silanol group. Therefore, the proton donor pre-associated silanol group is expected to be a more efficient nucleophile in the condensation process, giving rise to the observed phenomenon of intra-inter catalysis.

Our mechanistic interpretation of the kinetics assumes that the reactants in their ground states are not associated by the H-bond discussed above, which is reasonable in view of the generally lower values of the formation constants of H-bond complexes in  $\text{CH}_2\text{Cl}_2$  than those observed in  $\text{CCl}_4$ .

### Experimental Section

**Solvents.** Methylene chloride and carbon tetrachloride were purified by the method described in ref 42. Dioxane was purified as described in ref 43. Solvents were stored in ampules fitted with Teflon stopcocks.

**Catalyst.** Methanesulfonic acid and trifluoromethanesulfonic acid (Fluka) were freshly distilled on the high-vacuum line. Their solutions in methylene chloride were prepared according to the method described in ref 44.

**Model Siloxane Oligomers.** Siloxane oligomers were synthesized according to Scheme VI. (1,9-Dichlorodecamethyl)pentasiloxane (**15**) and (1,7-dichlorooctamethyl)tetrasiloxane (**16**)

Table VI  
Results of Simulation of Kinetics of Oligosiloxanol Condensation in CH<sub>2</sub>Cl<sub>2</sub><sup>a</sup>

compd	eq	k <sub>L</sub>	K <sub>E</sub>	K <sub>H</sub> , dm <sup>3</sup> ·mol <sup>-1</sup>
HO[SiMe <sub>2</sub> O] <sub>5</sub> H (1)	R = k[1] <sup>2</sup> [HA] <sub>0e</sub> (IX)	449 dm <sup>6</sup> ·mol <sup>-2</sup> ·s <sup>-1</sup>	10	500
	R = k[1][SiA][H <sub>2</sub> O] (XII)	22.5 dm <sup>6</sup> ·mol <sup>-2</sup> ·s <sup>-1</sup>	10	500
Me <sub>3</sub> Si[OSiMe <sub>2</sub> ] <sub>4</sub> OH (2)	R = k[2] <sup>2</sup> [HA] <sub>0e</sub> (IX)	2.54 dm <sup>6</sup> ·mol <sup>-2</sup> ·s <sup>-1</sup>	8	300
	R = k[2][SiA][H <sub>2</sub> O] (XII)	0.32 dm <sup>6</sup> ·mol <sup>-2</sup> ·s <sup>-1</sup>	8	300
Me <sub>3</sub> SiOSiMe <sub>2</sub> OH (3)	R = k[3] <sup>3</sup> [HA] <sub>0e</sub>	3.54 dm <sup>9</sup> ·mol <sup>-3</sup> ·s <sup>-1</sup>	5	150
	R = k[3] <sup>3</sup> [SiA][H <sub>2</sub> O]	0.71 dm <sup>9</sup> ·mol <sup>-3</sup> ·s <sup>-1</sup>	5	150

<sup>a</sup> Values of parameters k<sub>L</sub>, K<sub>E</sub>, and K<sub>H</sub> fitted for eq IX and XII.

were prepared by the method described in ref 45.

**Preparation of (1-Chloropentamethyl)disiloxane (17) and (1-Chloroundecamethyl)pentasiloxane (18).** Lithium trimethylsilanolate was prepared in situ by exploring the reaction described by Frye et al.<sup>46</sup> Methylolithium (17.6 g, 0.8 mol) in 500 mL of diethyl ether was introduced to octamethylcyclotetrasiloxane (59.2 g, 0.2 mol) in 200 mL of benzene. After about 0.5 h the solution of lithium trimethylsilanolate was transferred under a nitrogen atmosphere into a dropping funnel and added dropwise to 103 g (0.8 mol) of dimethyldichlorosilane in 200 mL of diethyl ether at -60 °C while the solution was vigorously stirred. Immediate formation of LiCl was observed. The mixture was allowed to warm to room temperature, filtered, and distilled, giving 58 g (70% yield) of 17, bp 120 °C. The GLC analysis showed no impurities.

In an analogous procedure, the reaction of 140 g (0.4 mol) of 16 with 0.25 mol of Me<sub>3</sub>SiOLi afforded 18, yield 61 g (0.15 mol) 60%, bp 125 °C (20 mmHg). GLC analysis indicated almost 100% purity.

**Preparation of Decamethylpentasiloxane-1,9-diol (1), Undecamethylpentasiloxan-1-ol (2), and Pentamethyl-disiloxan-1-ol (3).** A modified method of Andrianov et al.<sup>47</sup> was used. To a vigorously stirred solution of 17.5 g (0.22 mol) of pyridine and 4.0 g (0.22 mol) of water in 250 mL of diethyl ether at -5 °C was added a solution of 42.5 g (0.1 mol) of 15 in 50 mL of diethyl ether. The reaction mixture was allowed to warm to room temperature and filtered. The filtrate was washed with water and dried over CaCl<sub>2</sub>. The solvent was evaporated and the residual colorless fluid distilled on a high-vacuum line and kept over CaH<sub>2</sub> for 1 day. The product was then distilled again on the high-vacuum line into ampules fitted with Teflon stopcocks. 1 (23.5 g, 60% yield) was obtained. The GLC analysis showed small contamination (below 4%) with condensation and disproportionation products, which were taken into consideration in the kinetic studies.

In a similar procedure 2 (yield 70%, purity 98%) and 3 (yield 65%, purity better than 99%, bp 80 °C (50 mmHg)) were obtained as a result of the hydrolysis of 18 and 17, respectively.

**Preparation of (1-(Trifluoroacetoxy)pentamethyl)disiloxane (19).** 17 (3.66 g, 20 mmol) was introduced into 4.42 g (20 mmol) of CF<sub>3</sub>C(O)OAg in 20 mL of methylene chloride on a high-vacuum line. A solution of 19 in methylene chloride was obtained. The purity checked by GLC was better than 99%: <sup>1</sup>H NMR δ 0.0 (s, 9 H), 0.22 (s, 6 H); <sup>19</sup>F NMR δ (standard C<sub>6</sub>F<sub>6</sub>) 92.1 (s, 3 F).

**Kinetic Studies.** The condensation reactions of the model compounds in dioxane and methylene chloride were carried out under dry nitrogen in ampules fitted with Teflon stopcocks.

The reaction was started by introducing the desired amount of catalyst to the reagent solution. Samples were withdrawn at regular time intervals by means of hypodermic Hamilton syringes and quenched with pyridine (10% excess with respect to the catalyst). Concentrations of the substrate and products were determined by gas-liquid chromatography using an internal standard (*n*-undecane). In a separate experiment it was shown that no product of the reaction of the acid with the solvent is formed in a 0.1 mol·dm<sup>-3</sup> solution of CF<sub>3</sub>SO<sub>3</sub>H in dioxane containing 1 mol·dm<sup>-3</sup> water.

**Gas-Liquid Chromatographic Studies.** GLC analysis of the silylated sample was performed with a JEOL GLC 1100 chromatograph equipped with a TCD detector.<sup>48</sup> Typical conditions of analysis were as follows: 2 m × 3 mm steel column, packed with 10% OV-101 (poly(dimethylsiloxanes)) on Vavaport 30,

80/100 mesh was used. The column temperature was programmed at 15 °C/min. The injector and detector temperatures were 320 and 370 °C, respectively. The carrier gas was hydrogen with a flow rate of 40 mL/min. The stability of the stationary phase was tested once a week by performing an analysis of a mixture of pure linear oligomethylsiloxanes MD<sub>n</sub>M n = 0.1, ..., 10. The retention times of the model compounds were reduced by ~3% in 6 months, which indicates that the stability of the stationary phase during the analysis is quite good.

Peak assignments were done and molar response factors were determined with model compounds.

The silylation of the sample was performed with an excess of bis(trimethylsilyl)acetamide (BSA).

The reproducibility of the chromatographic data was satisfactory as checked by repetitive analysis and by agreement of the balance of substrates and products.

**IR Studies of Hydrogen Bonding.** Solutions of oligomers in CCl<sub>4</sub> for IR studies were prepared in a way analogous to those for the kinetic studies. Infrasil glass cells of various path lengths (0.2–0.025 cm) with tight Teflon stoppers were used. They were thoroughly rinsed with dry CCl<sub>4</sub> and then with a stream of pre-purified nitrogen before filling with the solutions. The spectra of model compound-solvent systems in the range 3000–3900 cm<sup>-1</sup> were recorded with a Perkin-Elmer 457 double-beam spectrophotometer with compensation for the solvent. The siloxanol concentrations were varied in the range 2 × 10<sup>-3</sup>–6 × 10<sup>-1</sup> mol·dm<sup>-3</sup>. The cell temperature was 35 °C.

**Computer Simulations of Kinetics.** The experimental data fit to the kinetic equations (IX–XII) was tested by simulating kinetic dependence for variable values of the parameters k<sub>L</sub>, K<sub>E</sub>, K<sub>H</sub>

$$\frac{d[4]}{dt} = k_L [1]_e^2 [HA]_{fe}^n \quad n = 1, 2 \quad (\text{IX})$$

$$\frac{d[4]}{dt} = k_L [1]_e^2 [H_2O]_e [HA]_{fe}^n \quad n = 1, 2 \quad (\text{X})$$

$$\frac{d[4]}{dt} = k_L [1]_e [SiA] [HA]_{fe}^n \quad n = 0.1, 2 \quad (\text{XI})$$

$$\frac{d[4]}{dt} = k_L [1]_e [SiA]_e [H_2O]_e [HA]_{fe}^n \quad n = 0.1, 2 \quad (\text{XII})$$

Stationary concentrations of the substrate [1]<sub>e</sub>, acid [HA]<sub>fe</sub>, ester [SiA]<sub>e</sub>, and water [H<sub>2</sub>O]<sub>e</sub> were assumed to be equilibrium concentrations of the esterification and H-bond formation found from

$$K_E = \frac{[SiA]_e [H_2O]_e}{[HA]_{fe} [SiOH]_e} \quad (\text{XIII})$$

$$K_H = \frac{[HA \cdots 1]_e}{[HA]_{fe} [1]_e} \quad (\text{XIV})$$

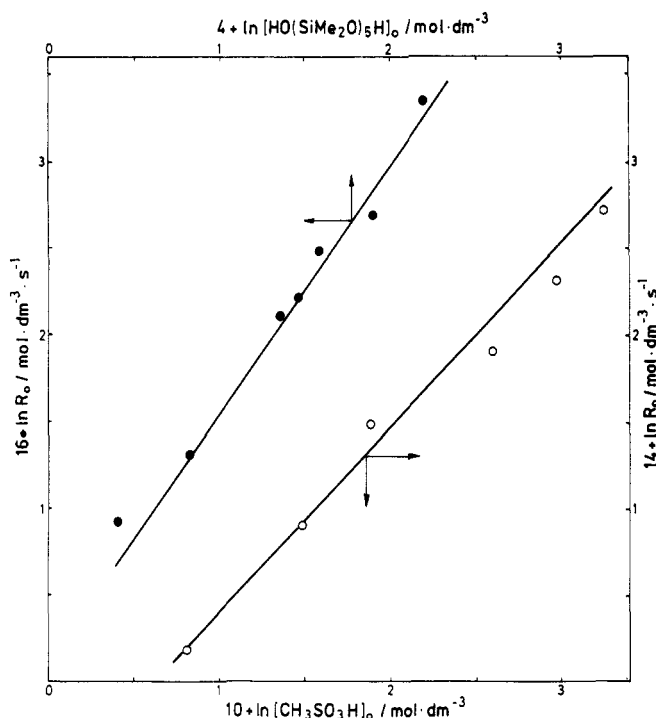
and using the balance equations

$$[HA]_0 = [HA]_{fe} + [SiA]_e + [HA \cdots 1]_e \quad (\text{XV})$$

$$[H_2O]_e = [H_2O]_0 + [SiA]_e \quad (\text{XVI})$$

$$2[1]_0 = 2[1]_e + [SiA]_e + [HA \cdots 1]_e \quad (\text{XVII})$$

A satisfactory agreement of the simulation with experimental data was achieved for eqs IX and XII. The values of the cor-



**Figure 13.** Fit of experimental data (points) to eq IX,  $n = 1$ ,  $k_L = 449 \text{ dm}^6 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$ ,  $K_E = 10$ ,  $K_H = 500 \text{ dm}^3 \cdot \text{mol}^{-1}$ .

responding parameters are given in Table VI. See also Figure 13.

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**Registry No.** 1, 7445-36-5; 2, 105247-76-5; 3, 56428-93-4; polybutadiene, 9003-17-2; poly(perdeuteriobutadiene), 29989-19-3; polystyrene, 9003-53-6; poly(perdeuteriostyrene), 27732-42-9.

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