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Behavior of Oligo(dimethylsiloxanols) in the Presence of Protic Acids in an Acid–Base Inert Solvent. Kinetics of the Competition of Disproportionation, Ester Formation, and Condensation

S. Rubinsztajn,[†] **M. Cypryk, and J. Chojnowski***

Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland

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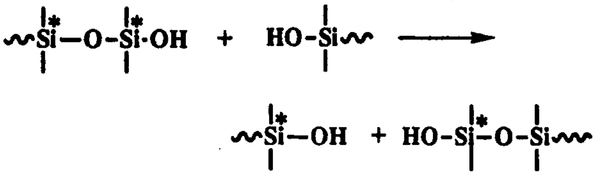
ABSTRACT: The kinetics of the acid-catalyzed disproportionation of α,ω-dihydroxyoligo(dimethylsiloxanes) $HO[SiMe_2O]_nH$, $n = 2, 5$, and their monohydroxyl analogues $Me[SiMe_2O]_nH$, $n = 2, 5$, were studied in methylene chloride. The kinetic rate law and mechanism are different from those found earlier for this reaction in dioxane. Two molecules of $HO[SiMe_2O]_5H$ participate in the formation of the transition state; water is not necessary to bring about the reaction. The siloxane bond cleavage is assisted by the silanol group located at the other end of the oligomer chain. Kinetics of the reaction are strongly affected by the conversion of the acid to a silyl ester group. The kinetics of this reversible esterification with trifluoroacetic acid were studied for $HO[SiMe_2O]_5H$ and $Me[SiMe_2O]_2H$. The reaction was found to be second order with respect to the acid. The apparent rate of the esterification was larger than the rate of disproportionation by a factor of 100. Intramolecular assistance by the silanol group was found to be important in the esterification process.

Introduction

Intense interest in the chemistry of oligosiloxanols has resulted from their role as intermediates in the synthesis of siloxane polymers and copolymers.[1–7] Hydroxy-terminated oligomers appear not only in systems of hydrolytic polycondensations of functional silanes but also in polymerizations of cyclic siloxanes.[8–10]

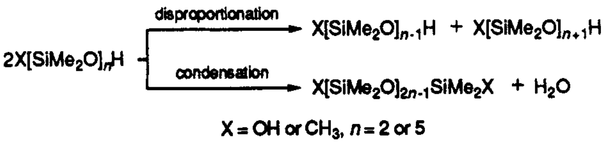
Previously we studied the kinetics of the acid-catalyzed condensation of linear oligo(dimethylsiloxanols) in methylene chloride (CH_2Cl_2) and in dioxane.[11] We found that this reaction was accompanied by specific interchain redistribution of ultimate siloxane units bearing the hydroxyl group according to eq 1. The kinetics of this redistribution have recently been examined in dioxane,[12,13] and we now report the extension of these studies to methylene chloride.



$$\sim\overset{|*}{\underset{|}{Si}}-O-\overset{|*}{\underset{|}{Si}}\text{-}OH + HO-\overset{|}{\underset{|}{Si}}\sim \longrightarrow \sim\overset{|*}{\underset{|}{Si}}-OH + HO-\overset{|*}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}\sim \quad (1)$$

The behavior of oligosiloxanols in the presence of acids in an acid–base inert solvent such as methylene chloride is quite different from that observed in a solvent able to act as a base, such as dioxane.[11] Methylene chloride is a convenient solvent to carry out heterofunctional polycondensation of oligosiloxanols[14,15] and is also the solvent in which the cationic polymerization of cyclic siloxanes has been broadly studied.[8,16–18] Thus, knowledge of the behavior of oligosiloxanol in this solvent is of particular interest. Reaction 1 may strongly contribute to the cationic polymerization of cyclic siloxanes and to the polycondensation of functional silanes involving the SiOH group.[11]

In this paper we present a detailed examination of the kinetics and the mechanistic analysis for the redistribution process in the presence of a strong or a moderately strong protic acid using model oligomers $HO[SiMe_2O]_nH$, $n = 2$ (**1**), $n = 5$ (**2**), and $Me[SiMe_2O]_nH$, $n = 2$ (**3**), $n = 5$ (**4**). The first step of the redistribution 1 is the disproportionation of the model oligomer which produces oligomers $n-1$ and $n+1$ (eq 2). The formation of disproportionation and condensation reactions according to eq 2 was monitored by gas–liquid chromatography in the initial period of the reaction, and initial rates of disproportionation and condensation were separately determined.



$$2X[SiMe_2O]_nH \begin{cases} \xrightarrow{\text{disproportionation}} X[SiMe_2O]_{n-1}H + X[SiMe_2O]_{n+1}H \\ \xrightarrow{\text{condensation}} X[SiMe_2O]_{2n-1}SiMe_2X + H_2O \end{cases} \quad (2)$$

$X = OH$ or CH_3, $n = 2$ or 5

The kinetics of both of these competitive reactions, condensation and disproportionation, are strongly affected by the reversible reaction of the acid with the oligosiloxanol, leading to the formation of the silyl ester end group according to eq 3. This reaction reduces the amount of the catalyst available for the promotion of reactions represented by eq 2. The esterification of model oligomers **2** and **3** with CF_3COOH in CH_2Cl_2 was followed by the infrared spectroscopy monitoring the O–H stretching band of the acid. Results of the investigation are discussed herein.

$$X[SiMe_2O]_nH + HA \overset{K_1}{\rightleftharpoons} X[SiMe_2O]_{n-1}SiMe_2A + H_2O \quad (3)$$

$$A = CF_3C(O)O,\ X = OH,\ n = 5\ (\mathbf{2})$$

$$A = CF_3C(O)O,\ X = Me,\ n = 2\ (\mathbf{3})$$

Results and Discussion

Disproportionation–Condensation Competition. Our previous studies[12] showed that in dioxane the dis-

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* To whom correspondence should be addressed.

[†] Present address: General Electric CR&D, Schenectady, NY 12301.

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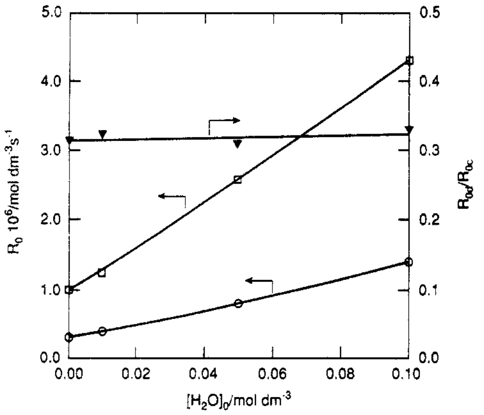


Figure 1. Effect of water introduced into the system on the initial rate disproportionation R_{0d} (○) and condensation R_{0c} (□) of decamethylpentasiloxane-1,9-diol (**2**) in methylene chloride in the presence of methanesulfonic acid at 35 °C. $[2]_0 = 0.1$ mol dm^{-3}, $[CH_3SO_3H]_0 = 1 \times 10^{-4}$ mol dm^{-3}. (▼) Ratio R_{0d}/R_{0c}.

Table I. Percent Disproportionation Product from the Reaction of Decamethylpentasiloxane-1,9-diol (2) Catalyzed by Protonic Acids in CH_2Cl_2 at 60% Conversion Depending on the Acid Strength at 35 °C

acid	relative strength in water	% disproportionation product
CF_3COOH	1	20
CH_3SO_3H	17	10
CF_3SO_3H	427	<2

proportionation of linear oligo(dimethylsiloxanols) occurs with involvement of water. Water cleaves the ultimate siloxane unit in the rate-determining step, producing reactive monomeric dimethylsilanediol, which undergoes subsequent condensation with another molecule of the oligomer.

In contrast to the behavior of oligo(dimethylsiloxanols) in dioxane, water produced in the acid-catalyzed condensation of these compounds in methylene chloride does not seem to participate in the reaction represented by eq 1. The disproportionation products appear at the beginning of the condensation process, and the initial rates of both disproportionation and condensation are affected to a similar extent by an introduction of small amounts of water to the system (Figure 1). This observation indicates that a substantial difference exists in mechanisms of the formation of the disproportionation products in the course of the acid-catalyzed condensations of oligosiloxanols in dioxane and in methylene chloride.

Three protic acids differing markedly in their strength were used as catalysts. The contribution from the disproportionation was found to increase with decreasing acid strength of the catalyst (Table I).

In dioxane, the acid–ester equilibrium according to eq 3 lies strongly to the side of the acid, which is effectively stabilized by strong hydrogen bonding to solvent molecules. In contrast, methylene chloride is an acid–base inert solvent unable to form an effective hydrogen bond with the acid. As a consequence, the thermodynamic reactivity toward the esterification is higher in this system and a considerable fraction of the acid is transformed into the ester.[19] This phenomenon makes the kinetics of disproportionation in methylene chloride more complicated than in dioxane. For simplification, in the first step of the kinetic analysis the effect of reaction 3 was neglected. The kinetic law was examined using the uninomial eq 4, by which the initial rate was correlated with total concentrations of the catalyst $[HA]_0$ and the substrate $[S]_0$ introduced to the system. Initial rates were determined as slopes at time zero of the disproportionation product formation–time curves, exemplified in Figure 2.

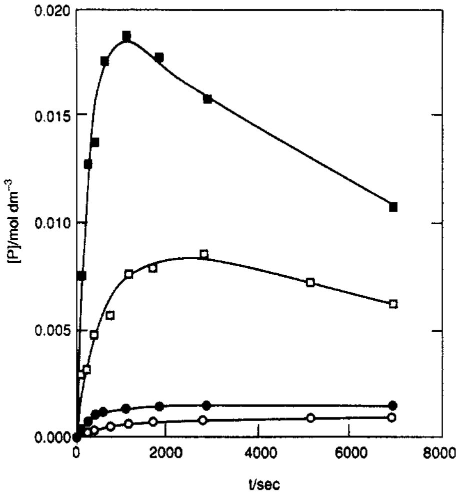


Figure 2. Comparison of the disproportionation and condensation reactions in the product formation–time dependencies in the reaction of tetramethyldisiloxane-1,3-diol (**1**) in methylene chloride in the presence of trifluoroacetic acid at 35 °C. $[CF_3COOH]_0 = 0.005$ mol dm^{-3}. $[1]_0 = 0.1$: disproportionation (○); condensation (□). $[1]_0 = 0.3$: disproportionation (●); condensation (■).

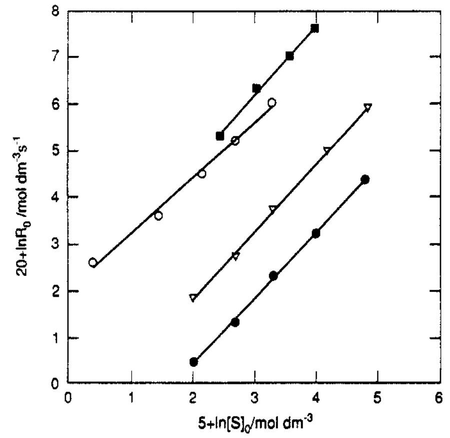


Figure 3. Dependence of the initial rate of the disproportionation R_0 of tetramethyldisiloxane-1,3-diol (**1**; ■), decamethylpentasiloxane-1,9-diol (**2**; ○), pentamethyldisiloxanol (**3**; △), and undecamethylpentasiloxane-1-ol (●), on the initial substrate concentration S_0 in methylene chloride in the presence of trifluoroacetic acid at 35 °C. $[CF_3COOH]_0 = 0.005$ mol dm^{-3}.

$$(d[P_d]/dt)_0 = k_1[HA]_0^{\,n}[S]_0^{\,m} \tag{4}$$

P_d is a disproportionation product.

The correlation of the rate with the substrate concentration is presented in Figures 3 and 4 for CF_3COOH and CH_3SO_3H, respectively, while the dependence of the initial rate on the catalyst concentration is shown in Figure 5. Values of the kinetic parameters for various substrates and acids are compared in Table II.

In the second approach, in which the acid–ester transformation was taken under consideration, the kinetic analysis was made only for trifluoroacetic acid for which silanol esterification (reaction 3) has been studied,[19] and the results will be discussed in the second part of this paper. This reaction occurs at a rate approximately 2 orders of magnitude higher than that of the oligomer condensation reaction under comparable conditions. Thus, as an approximation it may be assumed that the equilibrium 3 is established at the beginning of the condensation process and that the initial acid concentration is

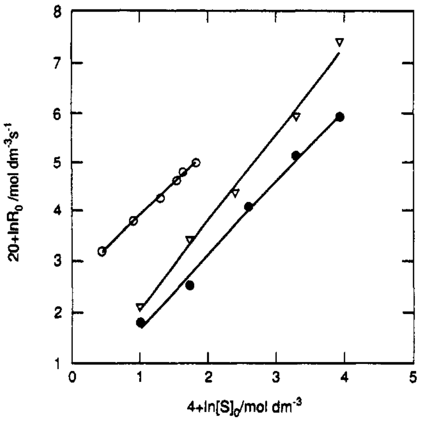


Figure 4. Dependence of the initial rate of the disproportionation R_0 of decamethylpentasiloxane-1,9-diol (**2**; ○), pentamethyldisiloxanol (**3**; △), and undecamethylpentasiloxane-1-ol (**4**; ●), on the initial substrate concentration S_0 in methylene chloride in the presence of methanesulfonic acid at 35 °C. $[CH_3SO_3H]_0 = 1 \times 10^{-4}$ mol dm^{-3}.

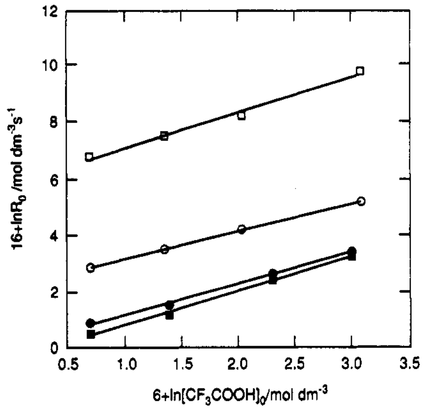


Figure 5. Dependence of the initial rates of condensation and disproportionation reactions R_0 of tetramethyldisiloxane-1,3-diol (**1**) and pentamethyldisiloxanol (**3**) in methylene chloride on the initial concentration of trifluoroacetic acid at 35 °C. $[1]_0 = 0.2$ mol dm^{-3}: condensation (□); disproportionation (○). $[3]_0 = 0.5$ mol dm^{-3}: condensation (■); disproportionation (●).

fully controlled by this equilibrium, i.e., is not affected by water produced in the condensation reaction. The value of the equilibrium constant K_1 for **2** was used on the basis of investigations described in the second part of this paper. True initial concentrations of the acid $[HA]_e$ and the substrate $[S]_e$ were calculated for every experimental point using eqs 5–8.

$$K_1 = \frac{[SiA]_e[H_2O]_e}{[HA]_e[S]_e} \tag{5}$$

$$[HA]_0 = [HA]_e + [SiA]_e \tag{6}$$

$$[SiA]_e = [H_2O]_e \tag{7}$$

$$[S]_e = [S]_0 - [SiA]_e \tag{8}$$

SiA is the ester formed from HA and S. The initial rate of the disproportionation product formation was correlated with calculated values of the true initial concentrations by uninomial eq 9.

$$(d[P_d]/dt)_0 = k_1'[HA]_e^{n'}[S]_e^{m'} \tag{9}$$

The correlation for substrates **1** and **3** is presented in Figures 6 and 7, and values of parameters are quoted in Table II. These data indicate that the order of the disproportionation of oligosiloxanols catalyzed with CF_3COOH is ca. 2.3 for **1**, **3**, and **4** and 1.9 for **2** with respect to the substrate, while the order in the acid is 0.6. The deviations from integer values are probably due to the second in the substrate and first in the acid for **2**. Although the true kinetic law for the reaction catalyzed with CH_3SO_3H was not determined, a close similarity of the apparent kinetic law for CF_3COOH and CH_3SO_3H (Table II) allows an assumption that in the case of the stronger methanesulfonic acid the true order of disproportionation of **2** is also second in the oligomer and first in the acid. Thus, unlike in dioxane, two molecules of the substrate appear in the transition state together with one molecule of the catalyst. Similarly, as in dioxane, the disproportionation pathway in CH_2Cl_2 involves proton transfer to the siloxane oxygen adjacent to the hydroxyl group. The proton transfer is likely to occur within a cyclic H-bonded complex of the acid and oligomer according to Scheme I. This mechanism is in agreement with the observed features of the reaction. Stronger acids, such as CH_3SO_3H and in particular CF_3SO_3H, show a lower ability to form the cyclic H-bond complex. Instead, these strong acids protonate the silanol group, which is more basic than the siloxane group,[11,20] favoring condensation. In dioxane the mechanism involving the cyclic H-bond complex does not operate because the solvent molecule forms an H-bond complex with silanol more readily than the acid.

An interesting observation is the considerable difference in the reactivity of oligo(siloxanediol) **2** and its homologue **4** having one silanol end group replaced by a methyl group. The diol reacts faster by a factor of about 10 if allowance is made for the statistical factor of 4. This result indicates that the silanol group present at the other chain terminus renders an assistance to the siloxane cleavage. Similar assistance was observed for the oligo(siloxanediol) condensation reaction in methylene chloride.[11] As shown in Chart I, one silanol functional group acts as a base receiving the incipient proton from a second silanol group, which attacks the electrophilic silicon center.

The increase in the order of the reaction with respect to the substrate observed in cases of oligomers having only one OH group (Table II) may be explained by assuming that the disproportionation is assisted by a similar intermolecular interaction involving a silanol group originating from another oligomer molecule (Chart I). Assistance by a siloxane group is also feasible but much less effective due to its lower basicity.[11] In dioxane this phenomenon of autocatalysis has not been observed for the condensation and disproportionation of oligosiloxanols because the incipient proton is received by the solvent molecule.[11,12]

Kinetics of Silanol Esterification. The reversible conversion of the silanol end group into an ester group by a protic acid strongly affects the course of acid-catalyzed polycondensation involving silanol by decreasing the actual catalyst concentration in these systems. This esterification is also important in ring-opening polymerization of cyclic siloxanes initiated by protic acids.[7,17] In the polymerization the esterification reaction controls concentrations of the silanol and ester end groups as well as concentrations of the acid and water. The silanol esterification has so far been studied only for the monomeric model $Me_3SiOH + CF_3COOH$ in CH_2Cl_2.[19] The equilibrium of this process was found to be strongly affected by hydrogen bonding and by the concentration of reactants. Previous work has shown that the esterification reaction proceeds faster than does silanol condensation in the same system. However,

Table II. Kinetic Parameters for the Disproportionation Reaction of Tetramethyldisiloxane-1,3-diol (1), Decamethylpentasiloxane-1,9-diol (2), Pentamethyldisiloxanol (3), and Undecamethylpentasiloxane-1-ol (4), Catalyzed with Trifluoroacetic and Methanesulfonic Acids (Equations 4 and 9) ($[CF_3COOH]_0 = 0.005$ mol dm^{-3}, $[CH_3SO_3H]_0 = 1 \times 10^{-4}$ mol dm^{-3})[a]

substrate	catalyst	k_1[b]	m	n	k_1'[c]	m'	n'
1	CF_3COOH	3.7×10^{-3}	1.5	1.0	5.9×10^{-2}	2.3	0.6
2	CF_3COOH	1.2×10^{-3}	1.2			1.9	
2	CH_3SO_3H	5.1×10^{-2}	1.3				
3	CF_3COOH	1.5×10^{-4}	1.45	1.1	1.1×10^{-3}	2.25	0.6
3	CH_3SO_3H	3.0×10^{-2}	1.7				
4	CF_3COOH	4.1×10^{-5}	1.35			2.25	
4	CH_3SO_3H	8.5×10^{-3}	1.45				

[a] Primed values are calculated regarding the esterification equilibrium. [b] [mol^{1-m-n} dm$^{3(m-n-1)}$ s^{-1}]. [c] [mol$^{1-m'-n'}$ dm$^{3(m'-n'-1)}$ s^{-1}].

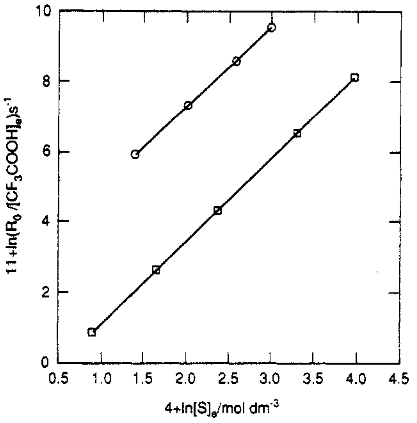


Figure 6. Dependence of the initial rate of the disproportionation of tetramethyldisiloxane-1,2-diol (1; ○) and pentamethyldisiloxanol (3; □) in methylene chloride in the presence of trifluoroacetic acid on the actual concentration of the substrate, allowing for the acid–ester equilibrium. Temperature 35 °C. $[CF_3COOH]_0 = 0.005$ mol dm^{-3}.

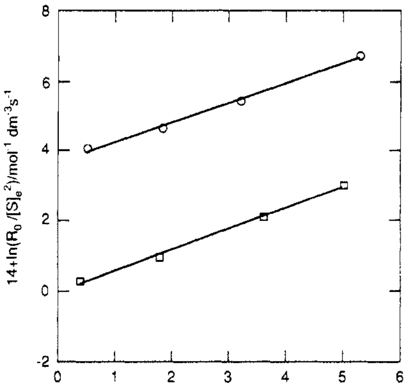


Figure 7. Dependence of the initial rate of the disproportionation R_0 of tetramethyldisiloxane-1,2-diol (1; ○) and pentamethyldisiloxanol (3; □) in methylene chloride in the presence of trifluoroacetic acid on the actual concentration of the acid, allowing for the acid–ester equilibrium. Temperature 35 °C. $[1]_0 = 0.2$ mol dm^{-3}; $[3]_0 = 0.5$ mol dm^{-3}.

the kinetics and mechanism of the esterification reaction have not been yet established because both the reactants (silanol) and product (silyl ester) are unstable. Moreover, its kinetics is very complex, being affected by the association state in the system and by accompanying reversible processes of condensation.

We approached these problems by investigation of esterification reactions of oligomers 2 and 3, as models of linear hydroxy-terminated poly(dimethylsiloxane), with CF_3COOH in methylene chloride. Although an acid of relatively low catalytic activity was used, the reaction in many cases was too fast to be investigated by a sampling technique. Infrared spectroscopic analysis permitted the reaction to be followed directly in an Infrasil glass cell at a low initial substrate concentration. Since the absorbance of the O–H stretching vibration band of uncomplexed CF_3COOH was monitored, additional determination of the constant of the acid–silanol hydrogen-bond complex formation was necessary. This constant was used to calculate the total acid and ester concentrations from the measured values of concentrations of uncomplexed CF_3COOH (see the Experimental Part). The ester formation vs time curves for oligomers 2 and 3 are compared in Figure 8, while the directly measured free acid concentration vs time curve for oligomer 2 is shown in Figure 9. At the beginning of the reaction, a fast decrease in the acid concentration was observed. After the concentration reached a minimum, the acid concentration slowly increased until the equilibrium conditions were reached. This behavior reflects the complex character of the process which occurs in this system. The equilibrium concentration of the ester and acid is established by three reversible reactions, eqs 10–12.

Condensation reactions proceeded more slowly than the esterification process, and the acid–ester equilibrium was slowly shifted toward the acid. The first portion of the

Scheme I

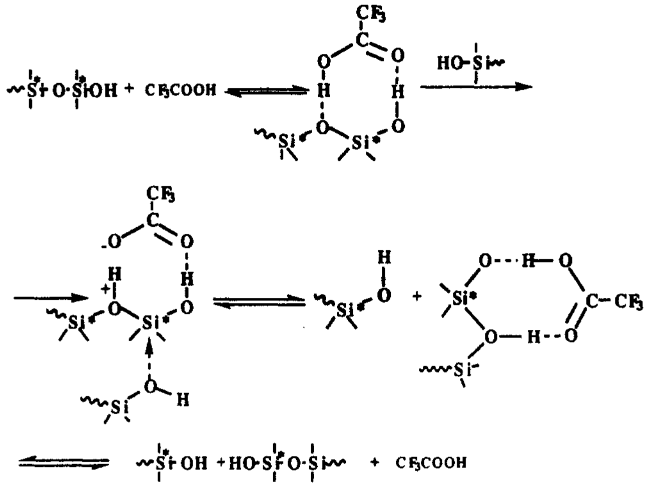
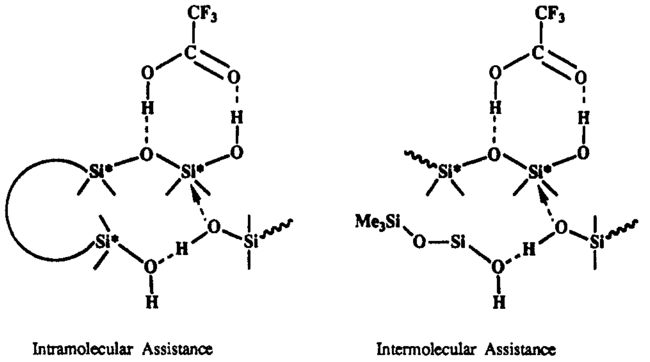


Chart I



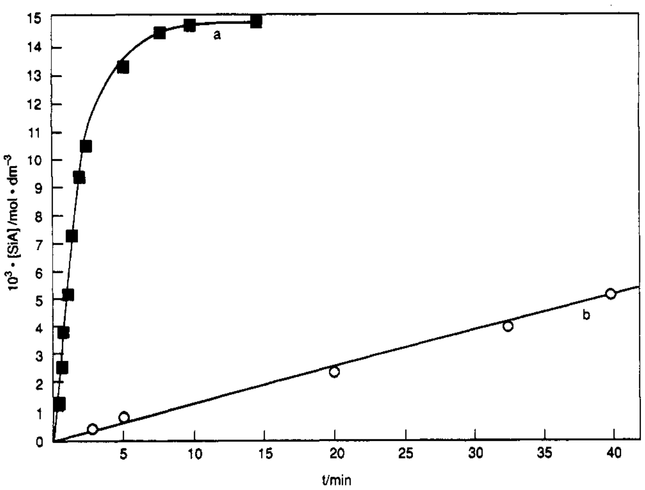


Figure 8. Ester formation–time dependencies for the reaction of decamethylpentasiloxane-1,9-diol (**2**; ■) and pentamethyldisiloxanol (**3**; ○) with trifluoroacetic acid in methylene chloride at 35 °C. $[CF_3COOH]_0 = 0.02$ mol dm^{-3}; $[\mathbf{2}]_0 = 0.02$ mol dm^{-3}; $[\mathbf{3}]_0 = 0.05$ mol dm^{-3}.

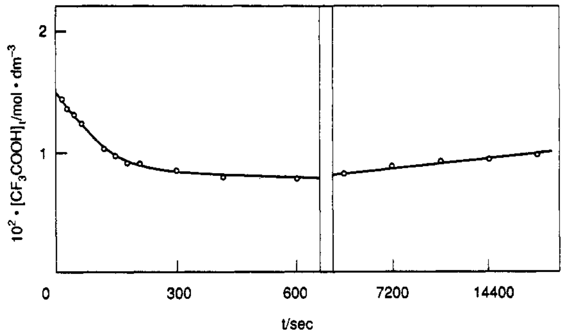


Figure 9. Variation of the concentration of uncomplexed CF_3COOH vs time as a result of its reaction with decamethylpentasiloxane-1,9-diol (**2**) in methylene chloride at 35 °C. $[CF_3COOH]_0 = 0.02$ mol dm^{-3}; $[\mathbf{2}]_0 = 0.01$ mol dm^{-3}.

$$CF_3COOH + HOSi{\sim}{\sim}{\sim} \rightleftharpoons CF_3C(O)OSi{\sim}{\sim}{\sim} + H_2O \tag{10}$$

$${\sim}{\sim}{\sim}SiOH + HOSi{\sim}{\sim}{\sim} \rightleftharpoons {\sim}{\sim}{\sim}SiOSi{\sim}{\sim}{\sim} + H_2O \tag{11}$$

$${\sim}{\sim}{\sim}SiOH + {\sim}{\sim}{\sim}SiOC(O)CF_3 \rightleftharpoons {\sim}{\sim}{\sim}SiOSi{\sim}{\sim}{\sim} + CF_3COOH \tag{12}$$

kinetic curve was only slightly perturbed by the condensation processes. The kinetic analysis was based on the initial rates, which were correlated with total initial concentrations by the uninomial eq 13. Statistical factor

$$\left(\frac{d[{\equiv}SiOC(O)CF_3]}{dt}\right)_{t=0} = sk_{obs}[\text{oligomer}]_{0,\text{total}}{}^{p}[CF_3COOH]_{0,\text{total}}{}^{q} \tag{13}$$

s equals 2 for oligomer **2** and 1 for oligomer **3**. The correlation according to eq 13 is shown in Figures 10 and 11 (hollow circles). Values of exponents *p* and *q* are given in Table III. They are fractional because the dependence is strongly affected by hydrogen-bonding association. In the second approach the hydrogen-bond complex formation was included. For each experimental point the initial concentration of free acid was determined by extrapolation to $t = 0$ of the uncomplexed acid concentration–time dependence as exemplified in Figure 9. Corresponding initial concentrations of the silanol were calculated from equations presented in the Experimental Part. The initial rate of the reaction was correlated with the initial silanol and acid concentrations according to eq 14. These

$$\left(\frac{d[{\equiv}SiOC(O)CF_3]}{dt}\right)_{t=0} = sk'[\text{oligomer}]_{0,\text{free}}{}^{p'}[CF_3COOH]_{0,\text{free}}{}^{q'} \tag{14}$$

correlations are shown in Figures 10 and 11 (filled circles). Values of exponents *p′* and *q′* quoted in Table III approach closer the true order of the reaction interpreted in terms of the number of molecules of the corresponding species participating in the transition state formation.[21] Thus,

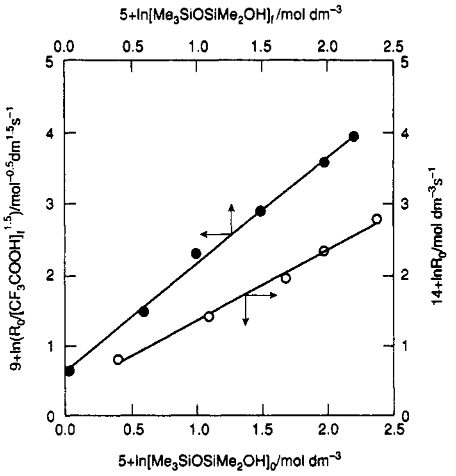


Figure 10. Dependence of the initial rate of the esterification R_0 of pentamethyldisiloxanol (**3**) with trifluoroacetic acid on the initial concentration of **3** in methylene chloride at 35 °C. $[CF_3COOH]_0 = 0.05$ mol dm^{-3}. (○) Using the total initial concentration. (●) Using the initial concentration of the uncomplexed substrate.

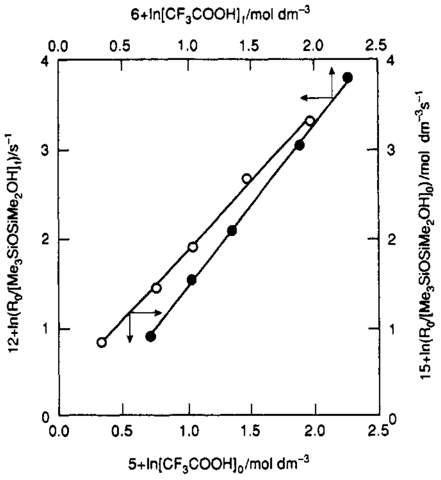


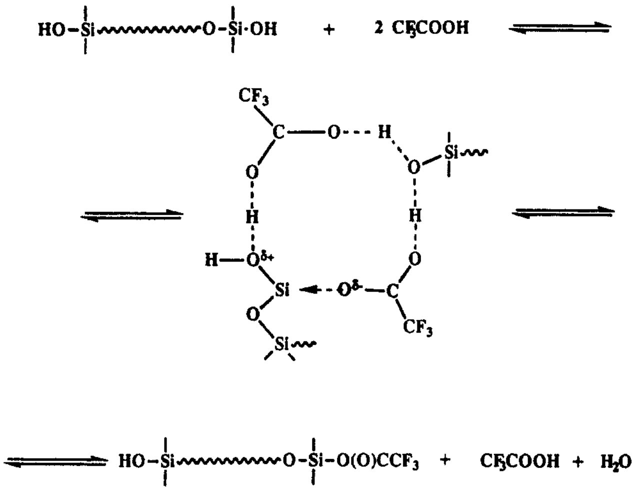
Figure 11. Dependence of the initial rate of esterification R_0 of pentamethyldisiloxanol (**3**) with trifluoroacetic acid on the initial acid concentration in methylene chloride at 35 °C. $[\mathbf{3}]_0 = 0.05$ mol dm^{-3}. (○) Using the total initial concentration. (●) Using the initial concentration of the uncomplexed substrate.

Table III. Kinetic Parameters of the Esterification of $Me_3SiOSiMe_2OH$ (3) and $HO(SiMe_2O)_5H$ (2) with CF_3COOH in CH_2Cl_2 at 35 °C[a]

comp	k_{obs}[b]	p	q	k'[c]	p'	q'
3	1.4×10^{-2}	0.9	1.5	1.38	1.5	1.8
2	1.9×10^{-2}	0.7	1.5	7.92	1.0	1.8

[a] Primed values are calculated regarding the concentrations of uncomplexed species. [b] [mol^{1-p-q} dm$^{3(p-q-1)}$ s^{-1}]. [c] [mol$^{1-p'-q'}$ dm$^{3(p'-q'-1)}$ s^{-1}].

Scheme II



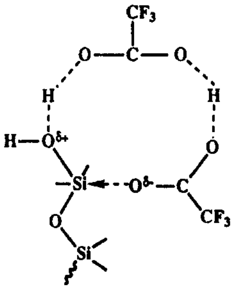
the order of the reaction with regard to the acid is second for both oligomers 2 and 3 pointing to the acid catalysis of the ester formation process. The esterification of 2 is first order in the oligomer, while the esterification of 3 shows the order 1.5 in silanol.

One of the most interesting observations was a considerable difference in reactivity between oligomers 2 and 3. Although the protonation of 3 should be easier than the protonation of 2, the latter underwent esterification much faster. This enhancement of the reactivity of the diol could be explained by the additional intermolecular catalysis of the process by the silanol group located at the other end of the chain. Thus the acid-catalyzed esterification–ester hydrolysis process in methylene chloride is also subjected to base assistance by the hydroxyl end group, similar to that observed in the condensation and disproportionation reactions of oligo(siloxanediols). This assistance seems to be a general phenomenon in the acid-catalyzed reactions of oligo(siloxanediols) in an acid–base inert solvent. An additional observation supporting this assistance is the elevation of the order of the esterification of 3. Since this oligomer has no silanol group at the other end of the chain, the catalysis may occur only intermolecularly, which should lead to the second order of the reaction in the oligomer. The observed fractional order points to competition with another pathway which does not involve the assistance of the hydroxyl group. A cooperative mechanism is proposed involving hydrogen-bond preassociation and a cyclic transition state formation (Scheme II). This mechanism accounts for all of the observed kinetic features of the reaction and is in agreement with the microreversibility rule which requires the same transition state structure for the reverse silyl ester hydrolysis process. A similar mechanism operates for the substrate 3. The only difference is that the silanol groups which appear in the transition state originate from two separate molecules of 3. However, in the case of the esterification of 3 a competitive pathway is also essential, which is proposed to involve the transition state (Chart II).

Conclusion

The kinetic rate law and mechanism of the acid-catalyzed disproportionation of α,ω-dihydroxyoligo(dimethylsiloxanes) in methylene chloride are different from those found for this reaction in dioxane. Two molecules of the decamethylpentasiloxane-1,9-diol participate in the formation of the transition state. The intra- or intermolecular assistance by a third silanol group plays an important role in the siloxane bond cleavage. This third silanol group acts as a base receiving a proton from the silanol group which attacks the silicon center. Kinetics of the reaction are strongly affected by the conversion of the acid to a silyl ester group. The esterification of model oligosiloxanols with trifluoroacetic acid was found to be second order with respect to the acid. The apparent rate of the esterification was larger than the rate of disproportionation by a factor of 100. Intramolecular assistance by the silanol group is also important in the esterification process. This assistance seems to be a common pattern in the acid-catalyzed processes of oligosiloxanols in acid–base inert solvent.

Chart II



Experimental Part

Substrates. Synthesis and purification of all oligo(dimethylsiloxanols) used as model substrates in kinetic studies are described in ref 12 and in earlier papers.[11]

Solvent. Methylene chloride (Fluka) was vigorously shaken with oleum for 24 h and repeatedly washed with a 5% water solution of Na_2CO_3 and then with water. It was dried with $CaCl_2$, refluxed with CaH_2, and twice distilled. Pure CH_2Cl_2 was stored under nitrogen in a dark ampule fitted with a Rotaflo stopcock from which it was distilled to a vessel in which solutions were prepared.

Catalysts. Methanesulfonic acid and trifluoromethanesulfonic acid (Fluka) were freshly distilled on a high-vacuum line into small thin-walled glass ampules of known weight. After having been filled, they were fused and weighed. To prepare the solution of the acid in methylene chloride, a small ampule of acid was placed in a closed vessel fitted with a Rotaflo stopcock containing a known amount of the solvent. The small ampule was crushed with a glass hammer. Operations were carried out either under high vacuum or in an atmosphere of an inert gas.

Kinetics of the Disproportionation and Condensation Processes. The kinetic studies of the disproportionation reactions were performed under an atmosphere of nitrogen in a thermostated ampule equipped with a Teflon stopcock. Solutions were prepared using 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 of the reaction. Samples were withdrawn at regular time intervals with a high-precision Hamilton syringe and introduced to a vessel containing an excess of a catalyst deactivating agent which also functioned as a trimethylsilylating agent. This agent was a 1:1 mol/mol mixture of Et_3N and either Me_3SiCl or BSA [bis(trimethylsilyl)acetamide]. The GLC analysis was performed with a Jeol JGC-1100 as described elsewhere.[11] Samples were not silylated in the cases of disproportionation of the oligomer 3. It was shown in a separate experiment that 3 and the products of its disproportionation could be analyzed directly by GLC.

Kinetics of the Esterification Process. The esterification reaction of 2 or 3 with CF_3COOH was performed in a thermostated Infrasil glass cell (0.1–1.0-cm path length) installed in a Perkin-Elmer IR spectrophotometer. The reaction was followed by recording of the spectra in the range of the free O–H stretching vibration band of CF_3COOH centered at about 3500 cm^{-1}. The calculation of the total concentration of the acid, i.e., both free and hydrogen-bonded, required the knowledge of the equilibrium constants of the complex formation according to eqs 15 and 16.

Table IV. Absorbance and Equilibrium Constants of Hydrogen-Bond Formation of $Me_3SiOSiMe_2OH$ (3) and $HO(SiMe_2O)_5H$ (2) with CF_3COOH in CH_2Cl_2 at 35 °C

$[3]_0$ (mol/dm^3)	$[CF_3COOH]_0$	$A_{t=0}$	K_1 (dm^3/mol)	$\bar{K}_1$ (dm^3/mol)
0.1500	0.050	0.25	19.2	
0.1250	0.050	0.28	19.9	
0.0940	0.050	0.30	27.0	
0.0720	0.050	0.35	23.4	23 ± 5
0.0510	0.050	0.40	26.4	
0.0204	0.050	0.56	19.7	

$[2]_0$ (mol/dm^3)	$[CF_3COOH]_0$	$A_{t=0}$	K_2 (dm^3/mol)	$\bar{K}_2$ (dm^3/mol)
0.020	0.020	0.17	80	
0.015	0.020	0.20	78	60 ± 20
0.010	0.020	0.24	47	
0.005	0.020	0.28	28	
0.002	0.020	0.29	56	

$$CF_3COOH + Me_3SiOSiMe_2OH \overset{K_1}{\rightleftharpoons} [CF_3OOH \cdots Me_3SiOSiMe_2OH] \quad (15)$$

$$CF_3COOH + HO(SiMe_2O)_5H \overset{K_2}{\rightleftharpoons} [CF_3COOH \cdots HO(SiMe_2O)_5H] \quad (16)$$

Complexes of the acid with the silanol group and with the siloxane group of the same species were not differentiated. The equilibrium constants were calculated using eqs 17 and 18.

$$K_n = \frac{[HA]_{total} - ([HA]_f + 2K_{HA\text{-}HA}[HA]_f^2)}{[HA]_f[S]_f} \qquad n = 1, 2 \quad (17)$$

$$[S]_f = [S]_{total} - [HA]_{total} - ([HA]_f + 2K_{HA\text{-}HA}[HA]_f^2) \quad (18)$$

$[HA]_{total}$ and $[HA]_f$ are concentrations of the total and free acid, respectively. $[S]_{total}$ and $[S]_f$ are concentrations of the total and free substrate, respectively. $K_{HA\text{-}HA}$ is the formation constant of the binary acid complex in CH_2Cl_2. The value 2.1 for 35 °C was taken from ref 21. The absorbance measured was corrected, allowing for the superimposed absorbance of complexes. Corrected absorbance values at the maximum of the band and calculated values of K_1 and K_2 are given in Table IV. Equations 15 and 16 were used to calculate $[HA]_{total}$ from the measured value of $[HA]_f$ for all experimental points. The ester concentration was $[HA]_0 - [HA]_{total}$ where $[HA]_0$ was the concentration of the acid introduced to the system.

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