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Condensation of model linear siloxane oligomers possessing silanol and silyl chloride end groups. The mechanism of silanol silylation by a chlorosilane in the presence of neutral nucleophiles

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Abstract

The condensation of pentamethyldisiloxane-1-ol (**1**) with 1-chloro-1-isopropyltetramethyldisiloxane (**2**) in methylene chloride solution has been studied as model of the polyheterocondensation of functional oligosiloxanes. The process catalysed by triethylamine, hexamethylphosphoroamide (HMPA) or some nitrogen heterocycles showed a high selectivity towards heterocondensation. Triethylamine promotes the reaction by acting as the base bonding to the incipient proton on the silanol group entering into the condensation. This mechanism of the catalysis by Et_3N was demonstrated by kinetic studies involving use of gas-liquid chromatography in conjunction with study of the hydrogen bonding by IR spectroscopy. In contrast, the kinetic data and the reactivity pattern indicate that *N*-heterocycles and HMPA catalyse the reaction by functioning as nucleophiles to form a transient complex with the chloride substrate. A mixture containing a highly nucleophilic *N*-heterocycle, triethylamine has no effect on the rate of the reaction, acting only as a HCl acceptor.

Introduction

Heterocondensation of functional silanes or functional siloxanes is widely used in synthesis of regular siloxane copolymers [1–5] and linear or cyclic siloxane oligomers [6,7]. The condensation of the silanol function with the chlorosilane function has been often exploited for this purpose [1,2,6,7]. However, when this reaction is applied to polysiloxanes, it is accompanied by cleavage of a siloxane bond [8,9], silanol homocondensation [9,10], and interconversion of the functional groups [10,11]. An effective way of increasing the selectivity of the heterocondensation

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seems to be to used uncharged Lewis bases as catalysts. Catalysis with a protonic acid or a strong base not appropriate for this purpose since it promotes homocondensation and interchain exchange [10,11].

The aim of the present work was to determine the effectiveness of the catalysis by uncharged nucleophiles in the condensation of a model oligosiloxanol with a model silyl chloride-ended oligosiloxane. We considered oligomers to be more appropriate models than simple silanes for studies of the condensation step in a siloxane polymer system. Some nitrogen heterocycles, an aliphatic amine, and a phosphorus oxide were chosen as the catalysts of the process.

The mechanism of this catalysis represents another interesting feature. The reaction studied may be also regarded as a silanol silylation by a chlorosilane (eq. 1).

$$-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{Cl}+\mathrm{HO}\overset{|}{\underset{|}{\mathrm{Si}}}-\xrightarrow{\text{N-base}}-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{O}\overset{|}{\underset{|}{\mathrm{Si}}}-+\mathrm{HCl}\qquad(1)$$

The catalytic action of uncharged nucleophiles, particularly nitrogen bases, proved to be very effective in the silylation of protic substrates with chlorosilanes and the mechanism of this catalysis has recently attracted considerable attention [12–17]. Although the prevailing view is that nitrogen bases act as catalysts by nucleophilic attack at silicon, their possible role as Brönsted bases that increase the nucleophilicity of the silylated reactant is unclear, and they are regarded as HCl-acceptors, providing no base-catalysis. Since silanols have relatively high acidities [18] this type of base catalysis might be expected in the system studied here. Such catalysis has been often considered for similar solvolytic processes [19–22].

Results and discussions

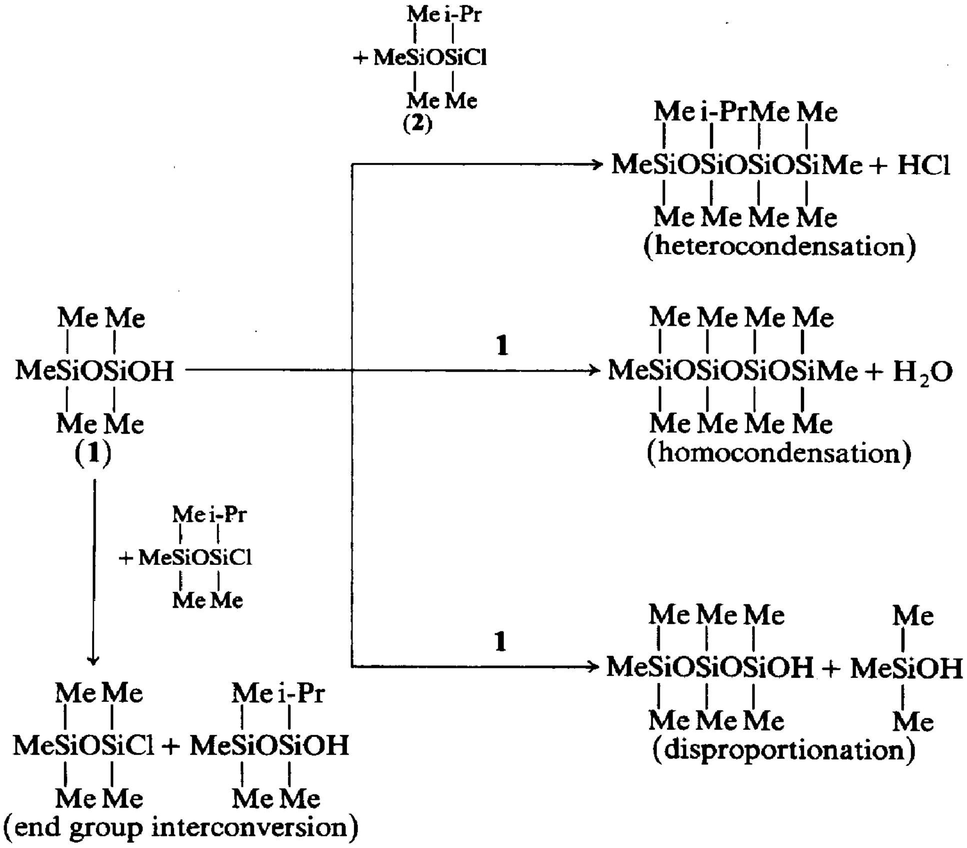
The selectivity of the process

The reaction of 1,1,2,2,2-pentamethyl-disiloxane-1-ol (**1**) with 1-chloro-1-isopropyl-1,3,3,3-tetramethyl-disiloxane (**2**) was studied as a model of the polyheterocondensation of silanol and silyl chloride-ended polysiloxanes. The reaction was carried out in methylene chloride solution in the presence of various catalysts. It was monitored by gas-liquid chromatography analysis of samples. The models chosen allowed distinction between the primary competing reactions which are: heterocondensation, oligosiloxanol homocondensation, and oligosiloxanol disproportionation, as depicted in scheme 1. The interconversion of the end groups might also occur to some extent, however in this system it was slowed down by a bulky isopropyl group.

The data presented in Table 1 demonstrate that the outcome of the reaction depends markedly on the catalyst used. In the presence of a strong acid like CF_3SO_3H the primary heterocondensation is minor compared with the homocondensation and disproportionation processes, whereas in the presence of triethylamine or *N*-heterocycles heterocondensation is strongly favoured occurring almost exclusively.

Kinetics of the process involving a single catalyst

The kinetics of the heterocondensation of **1** with **2** were studied to provide information on the catalytic activity of the bases used to promote the process and



Scheme 1

on the mechanism of the reaction. Since the catalyst acts as an HCl acceptor, it must be present in the system in a concentration at least equal to that of the Cl substrate. Initial rates of the heterocondensation in the presence of various catalysts were compared. The results are shown in Table 2.

Table 1

Data for the heterocondensation of model Cl–Si≡ and HO–Si≡ oligosiloxanes **2** and **1**, respectively, in CH_2Cl_2, at 25 °C. Initial concentrations $[\mathbf{1}]_0 = [\mathbf{2}]_0 = 0.200$ mol dm^{-3}. Quenching after 80–90% conversion of **2**

Catalyst	Catalyst concentr. in mol dm^{-3} (initial)	relative molar conversion of **2** per mole of converted **1**	Yield of products as mol % of the converted oligomer **1**		
			Hetero-condensation	Homo-condensation	Others (involving disproportionation or end group exchange)
CF_3SO_3H	1.00×10^{-3}	0.125	0.5	31	68.5
Et_3N	0.200	1	95	0	5
Et_3N + DMAP	$0.200 + 1.00 \times 10^{-2}$	0.98	98	0	2

[a] Some products of the primary homocondensation cannot be distinguished from secondary products involving the end group interconversion.

Table 2

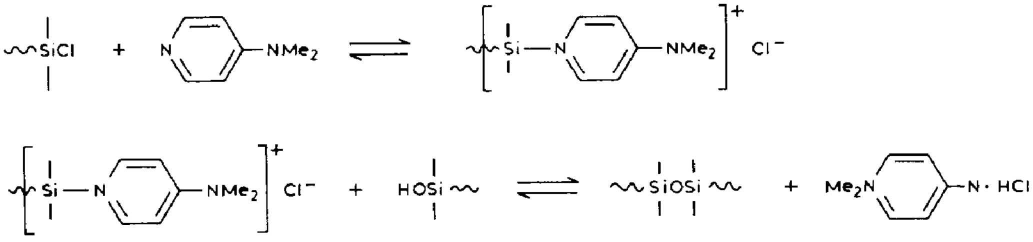
Comparison of catalytic activities of various organic bases in the heterocondensation of model Cl–Si≡ and HO–Si≡ oligosiloxanes **2** and **1**, respectively. Solvent CH_2Cl_2 at 25 ° C. Initial concentrations, $[\mathbf{1}]_0 = [\mathbf{2}]_0 = [\text{catalyst}]_0 = 0.200$ mol dm^{-3}

Catalyst	k (catalytic constant) (mol^{-2} dm^6 s^{-1})	Initial rate R_0 (mol dm^{-3} s^{-1})	$R_0/R_0(Et_3N)$	pK_B
Et_3N	5.15×10^{-4} [a]	7.2×10^{-6}	1	3.30
DMAP	2.86	2.30×10^{-2}	3200	4.30
Imidazole	1.18	9.4×10^{-4}	1300	6.97
NMI	0.84	6.7×10^{-3}	930	7.10
HMPA	3.6×10^{-2}	2.9×10^{-4}	40	
Pyridine	5.8×10^{-2}	4.6×10^{-4}	64	8.85

[a] In mol^{-1} dm^3 s^{-1}. NMI = *N*-methylimidazole.

The rate of the process depends strongly on the catalyst used. Without any catalyst the reaction is at first extremely slow, and is probably promoted by traces of HCl formed by hydrolysis of **2** by traces of water. The catalytic activity of triethylamine, the strongest base among the catalysts used, is low compared with that of the nitrogen heterocycles which have a low basicity and a high nucleophilicity, such as pyridine, 2-methylimidazole, and 4-(dimethylamino)pyridine (DMAP). This points to a nucleophilic character of the catalysis, at least in the case of strongly nucleophilic *N*-heterocycles and of phosphorus oxides. Nucleophilic catalysis has been observed in the somewhat related reactions involving alcoholysis of chlorosilanes [16] and silanethiols [23].

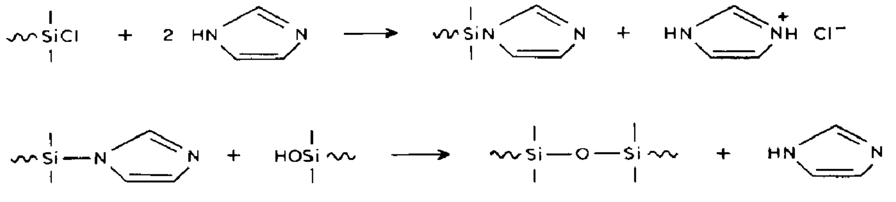
The most probable mechanism of this heterocondensation process is one involving formation of an ionic complex, as in eq. 2.



(2)

Recently the isolation of 1/1 ionic complexes of trimethylsilyl chloride and a *N*-nucleophile has been reported [17,24]. The role of these complexes as intermediates in the silylation reaction has been often discussed [12,14–17,23].

In the case of catalysis by primary or secondary amines the mechanism is likely to involve an intermediate silylamine.



(3)

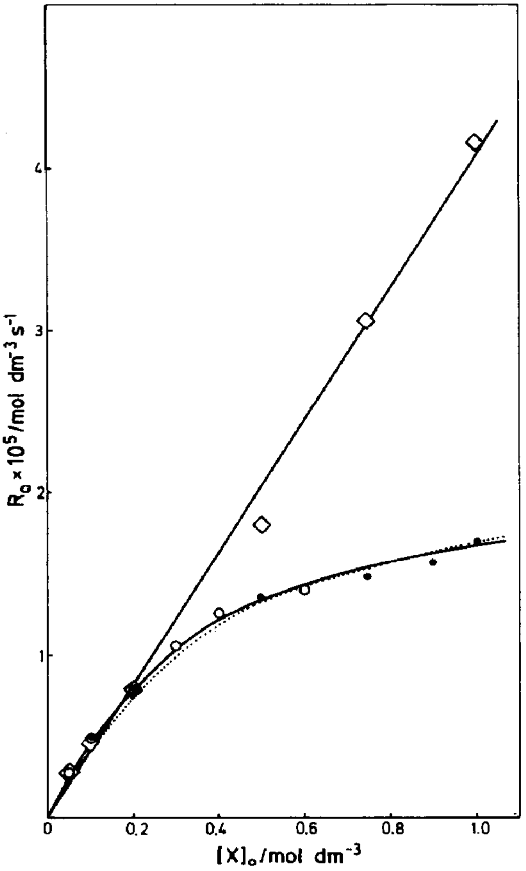
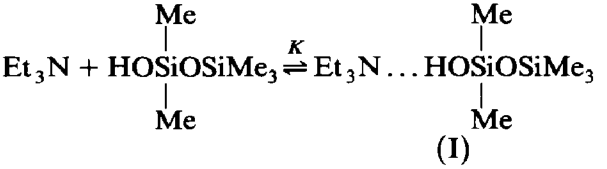


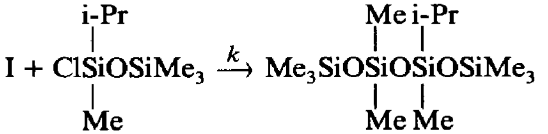
Fig. 1. The dependence of the initial rate, R_0, of the heterocondensation of **1** and **2** on the initial concentrations $[X]_0$ of **1**, ○ ($[2]_0 = [Et_3N]_0 = 0.200$ mol dm^{-3}); **2**, ◇ ($[1]_0 = [Et_3N]_0 = 0.200$ mol dm^{-3}); Et_3N, ● ($[1]_0 = [2]_0 = 0.200$ mol dm^{-3}). Continous lines represent the least square lines taking account of all the experimental points for the three series. Dotted line represents the similated dependence on the assumption that binary hydrogen-bonding complex $\equiv SiOH \cdot NEt_3$ is the species reacting with **2**, using the value of the complex formation constant determined from IR studies.

Series of runs were performed with equimolar initial amounts of **1**, **2**, and the catalyst. They revealed that the reaction showed third order kinetics to a high degree of the conversion with pyridine as the catalyst. However, with triethylamine serious deviations from the third order behaviour were observed, which implies that there is a fundamental difference between the mechanisms of the catalytic action of these two types of heterocondensation promoters.

More detailed kinetic studies were performed with the triethylamine system. The dependence of the initial rate on the concentrations of the two substrates and the triethylamine was studied in three independent series of runs. In each series the initial concentration of one component was varied while the initial concentrations of the remaining two components were kept constant at 0.200 mol dm^{-3}. The results are presented in Fig. 1. The linear increase in the initial rate with increasing concentration of the Cl-oligomer shows that, as expected, the reaction is of first order with respect to this substrate. On the other hand the plots for the reactions in which the initial concentration of the catalyst or the HO-substrate were varied, both show a similar and complex shape, with the rate tending, have to level-off at higher concentrations. Such behaviour implies the formation of 1/1 complex between the amine and the oligosiloxanol, presumably a hydrogen-bonded adduct, which is the actual species that reacts with the chlorooligosiloxane. The reaction scheme is as shown in eq. 4 and 5.



$$Et_3N + HO\overset{Me}{\underset{Me}{Si}}OSiMe_3 \overset{K}{\rightleftharpoons} Et_3N\ldots \underset{(I)}{HO\overset{Me}{\underset{Me}{Si}}OSiMe_3} \qquad (4)$$



$$I + Cl\overset{i\text{-}Pr}{\underset{Me}{Si}}OSiMe_3 \xrightarrow{k} Me_3SiO\overset{Me}{\underset{Me}{Si}}O\overset{i\text{-}Pr}{\underset{Me}{Si}}OSiMe_3 \qquad (5)$$

In order to confirm this proposal IR spectroscopic studies of hydrogen bonding between the oligosiloxanol and triethylamine in the reaction system were carried out. The absorbance at the maximum of the band corresponding to the ν(OH) vibration of free (uncomplexed) species was measured for series of solutions of Et_3N and **1** of different concentrations in methylene chloride. The complex formation constant was calculated from equation 6, where A_0 = absorbance of **1** in

$$K = \frac{A_0 - A}{\left(A[NEt_3]_0 - \frac{A_0 - A}{\epsilon\, l}\right)} \qquad (6)$$

CH_2Cl_2; A = absorbance of **1** at the same concentration in CH_2Cl_2 with Et_3N added; ϵ = molar absorbance coefficient of **1** and l = path length in cm. The results are presented in the Table 3.

Initial concentrations of the hydrogen-bonded complex of Et_3N with **1** were calculated for all kinetic runs, and initial rates were correlated with these concentra-

Table 3

Determination of the formation constant of the hydrogen-bonded adduct between oligosiloxanol **1** and triethylamine in CH_2Cl_2 at 25 °C.

No	$[\mathbf{1}]_0$	$[NEt_3]_0$	$A(OH_{free})$ [a]	K [b]
1	0.0405	0.0303	0.873	4.1
2	0.0405	0.0505	0.804	4.6
3	0.0405	0.0707	0.772	4.1
4	0.0405	0.101	0.696	4.4
5	0.0405	0.151	0.605	4.4
6	0.200	0.050	0.299	4.2
7	0.200	0.100	0.261	4.4
8	0.200	0.150	0.233	4.4
9	0.200	0.200	0.208	4.4
10	0.200	0.400	0.146	4.1

[a] $\epsilon(OH_{free})$ 123 dm^3 mol^{-1} cm^{-1}; path length was 0.2 mm for **1–5**, 2 mm for **6–10**. [b] In dm^{-3} mol^{-1}, $K = [\equiv SiOH\ldots NEt_3]/[SiOH]_f[NEt_3]_f = 4.4$ dm^3 mol^{-1}.

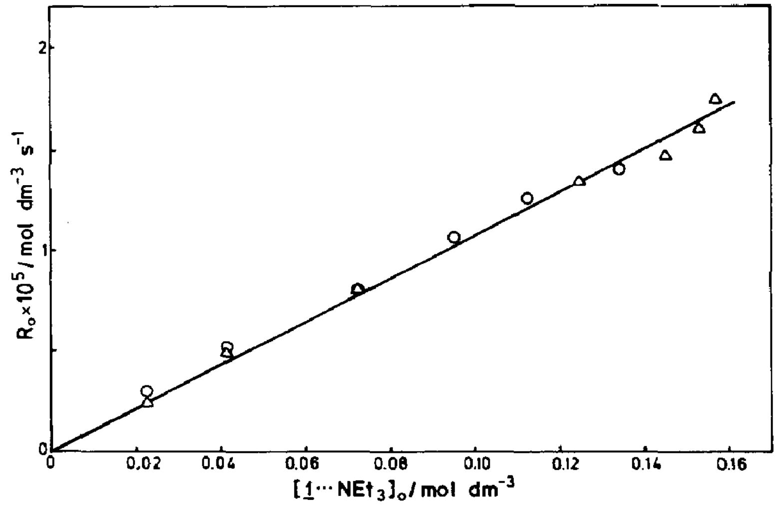
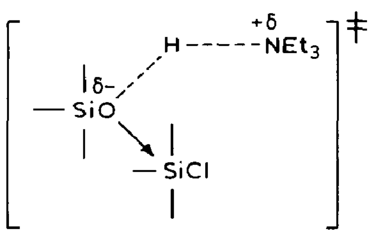


Fig. 2. The dependence of the initial rate R_0 on the complex ≡SiOH·NEt$_3$ initial concentration for the heterocondensation of **1** and **2**. △, series with variable concentration of Et$_3$N ([**1**]$_0$ = [**2**]$_0$ = 0.200 mol dm^{-3}); ○, series with variable concentration of **1** ([Et$_3$N]$_0$ = [**2**]$_0$ = 0.200 mol dm^{-3}).

tions (Fig. 2). Points for both series, one with variable [Et$_3$N]$_0$ and the other with variable [**1**]$_0$, lay well about the same straight line, indicating that the reaction is of first order with respect to the hydrogen-bonded complex.

The dependence of the initial rate on the silanol or Et$_3$N concentration was simulated in accord with eqs. 4 and 5 by using the value of $K = 4.4$ dm^3 mol^{-1} determined from the IR studies and the value of k of 5.2×10^{-4} mol^{-1} dm^3 s^{-1} determined from the slope of the plot in Fig. 2. The experimental values lie close to the curve from the simulation (Fig. 1).

Triethylamine thus functions in this system as a Brönsted general base to accept the proton from the oligosiloxanol in the rate-determining step (transition state **A**). To our knowledge this is the first case in which it has been possible to distinguish between base catalysis and nucleophilic catalysis in an amine-promoted silylation.



(**A**)

Kinetics of the reaction involving a combined base-nucleophile catalysis

The nitrogen base acts in this type of system both as the catalyst and as a proton acceptor. Thus a system containing two suitable bases should be very efficient. One of them, possibly a strong base used in a mole concentration equivalent to that of

Table 4

The dependence of the initial rate of the heterocondensation of model Cl–Si≡ and HO–Si≡ oligosiloxanes **2** and **1**, respectively, on the initial concentrations of triethylamine, **1**, and the **1**-NEt$_3$ complex. In CH$_2$Cl$_2$ at 25 °C, Initial concentraiton of [**2**], 0.200 mol dm^{-3}.

[**1**]$_0$ (mol dm^{-3})	[NEt$_3$]$_0$ (mol dm^{-3})	[≡SiOH...NEt$_3$]$_0$	$R_0 \times 10^5$
0.200	0.050	0.0220	0.255
0.050	0.200	0.0220	0.280
0.100	0.200	0.0411	0.490
0.200	0.100	0.0411	0.480
0.200	0.200	0.0720	0.790
0.300	0.200	0.0949	1.050
0.400	0.200	0.112	1.250
0.200	0.500	0.125	1.350
0.60	0.20	0.1344	1.400
0.20	1.00	0.1575	1.730

hydrolysable chloride, could function as the acid acceptor, and the other, possibly a weak base but a very efficient nucleophile, could act as a nucleophilic catalyst. This concept has previously been applied in some silylation processes [25], but there have been no kinetic studies of the mechanism operating in such a system.

A series of runs was performed involving equal initial concentrations of triethylamine, **1** and **2** in the presence of various catalytic amounts of DMAP or imidazole. The reaction obeyed the second order kinetic law to a high degree of conversion, indicating that Et$_3$N does not participate in the formation of the transition state, or more precisely that the catalysis by DMAP or imidazole is greatly predominant, as expected. The important observation is that the nucleophilic catalyst is not used up as the reaction proceeds, which means that the role of HCl acceptor is played only by Et$_3$N, as in eq. 7.

$$\begin{array}{c} \mathrm{Et_3N_{(liq)}} + \mathrm{DMAP \cdot HCl_{(liq)}} \rightleftharpoons \mathrm{Et_3N \cdot HCl_{(liq.)}} + \mathrm{DMAP_{(liq.)}} \\ \downarrow \\ \mathrm{Et_3N \cdot HCl_{(solid)}} \end{array} \tag{7}$$

The plot of the specific rate on the concentration of DMAP and imidazole is a straight line passing through the origin (Fig. 3), confirming that any contribution from catalysis by Et$_3$N may be neglected, and that the *N*-heterocycle is the true catalyst, and the kinetic equation is that shown in eq. 8

$$-\frac{\mathrm{d}[\mathbf{2}]}{\mathrm{d}t} = k \cdot [\mathrm{DMAP}][\mathbf{1}][\mathbf{2}] \tag{8}$$

It should be noted that in the series with DMAP as catalyst some runs were carried out with two different initial concentrations of triethylamine. The points for the two concentrations fell on the same line (Fig. 3), confirming that the hydrogen bonding with Et$_3$N does not affect the reactivity of the oligosiloxanol, i.e. the free species and the hydrogen-bonded oligosiloxanol react at the same rate. Limiting cases for the hydrogen bond or free species as exclusive reactants are shown in the Fig. 3.

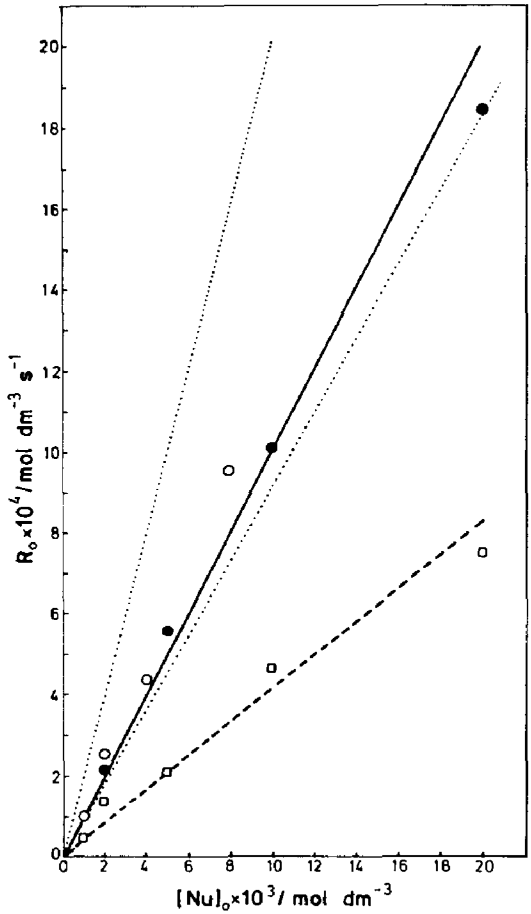


Fig. 3. The dependence of the heterocondensation of **1** and **2** in the presence of the Et_3N + nucleophile catalytic system on the concentration of the nucleophile: DMPA (cont. line) and imidazole (dashed line). $[\mathbf{1}]_0 = [\mathbf{2}]_0 = 0.200$ mol dm^{-3} ●, $[Et_3N]_0$ 0.100 mol dm^{-3} (DMAP); ○, $[Et_3N]_0$ 0.200 mol dm^{-3} (DMAP); □, $[Et_3N]_0$ 0.200 mol dm^{-3} (imidazole). The dotted lines represent the limiting cases for $[Et_3N]_0$ 0.200 mol dm^{-3} if only the hydrogen-bonded complex entered the reaction (upper line), or if only the uncomplexed silanol reacted (lower line), the rate constant calculated from points corresponding to $[Et_3N]_0$ 0.100 mol dm^{-3} being used.

The above results show that catalysis by uncharged bases in chlorine-displacement from silicon can take various forms, depending on the structure and the conditions.

Experimental

Solvent. Methylene chloride (Fluka) was purified as described in ref. 26. The solvent was stored in an ampoule fitted with Teflon stopcocks.

Catalyst. Pyridine, *N*-methylimidazole and HMPA (Aldrich Chem. Co.) were distilled from CaH_2. Triethylamine was distilled from P_2O_5. Imidazole (Aldrich Chem. Co.) was sublimed on the high-vacuum line. DMAP (Aldrich Chem. Co.) was recrystallised from pentane and dried on the high-vacuum line. Solutions of these catalysts in methylene chloride were prepared under dry nitrogen. Trifluoromethanesulfonic acid (Fluka) was freshly distilled on the high-vacuum line. Its solution in methylene chloride was prepared by the method described in ref. 27. All the catalysts or their solutions were stored in ampoules fitted with Teflon stopcocks.

Model compounds

1,1,3,3,3-Pentamethyldisiloxane-1-ol (**1**) was prepared by the method described in ref. 8.

1-Chloro-1-isopropyl-1,3,3,3-tetramethyldisiloxane (**2**) was made by reaction of dichloromethylisopropylsilane with lithium trimethylsilanolate as described in ref. 9. The product mixture was distilled, to give 25 g (65% yield) of **2**, b.p. 38 °C/18 mmHg.

The purities of all model compounds were carefully checked by gas liquid chromatography.

Kinetic studies

Kinetic runs were carried out under dry nitrogen in ampoules fitted with Teflon stopcocks. Solutions of the reagents in CH_2Cl_2 were prepared using Hamilton hypodermic syringes. The reaction was followed by GLC determination of the substrate and products concentrations with undecane as internal standard. GLC analyses were performed with a JEOL GLC 1100 FTP chromatograph equipped with a TCD detector, as described in ref. 28. Peak assignments were made and molar response factors determined by use of model compounds. The chromatographic data were satisfactory reproducible as shown by repetitive analyses and by the satisfactory mass balance between substrates and products.

Studies of the hydrogen-bond complex

All operations were performed under dry nitrogen. Solutions for IR studies were prepared in the way described for kinetic studies. Infrasil glass cells of 0.2–0.02 cm path lengths with tight Teflon stoppers were used. The spectra of solutions of model compound **1** along with triethylamine in CH_2Cl_2 in the range 3900–3000 cm^{-1} were recorded on a Specord M80 double-beam spectrophotometer with compensation for the solvent. The siloxanol concentrations were varied over the range 0.0405–0.2 mol dm^{-3} the triethylamine concentrations over the range 0.01–0.4 mol dm^{-3}. The cell temperature was 25 °C.

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