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Kinetics of the condensation of oligosiloxanes containing acetoxyl and hydroxyl end groups catalyzed by uncharged nucleophiles in an acid–base inert solvent

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Abstract

Condensation of undecamethylpentasiloxane-1-ol (**1**) with 1-acetoxypentamethyldisiloxane (**2**) in methylene chloride in the presence of uncharged bases has been studied as a model for the coupling of acetoxyl and hydroxyl ended polydimethylsiloxane chains. Triethylamine acts not only as the acceptor of the acid released in the process but also as a Brönsted base catalyst activating silanol group. However, weakly basic but strongly nucleophilic *N*-hetercycles such as 4-dimethylaminopyridine are more effective catalysts promoting the condensation by acting as nucleophiles to activate the acetoxysilane.

Introduction

Recently we presented results of a kinetic study of the condensation of oligosiloxanes containing silanol and silyl chloride end groups, and pointed out the effectiveness of the catalysis by uncharged bases such as amines, some nitrogen heterocycles, and oxyphosphoryl compounds [1]. We thought it would be of interest to extend these studies to silanol-acetoxysilane condensation system, a reaction often used in the synthesis of polysiloxanes [2]. The main use of silanol-acetoxysilane condensation is in the construction of a polysiloxane network in room temperature vulcanization of the RTV silicone rubber [2,3]. This reaction was also of interest as a possible route to siloxane copolymers having various side groups or siloxane sequences regularly arranged along the chain. There is considerable interest in the synthesis of such copolymers [4–7].

Another objective of this research was to study the scope of catalysis by uncharged nucleophiles in substitution at silicon atom and to throw light on the mechanism of this catalysis. Silanolysis of acetoxysilanes is of interest in this respect because it involves a poor leaving group. Ionization leading to the formation of a

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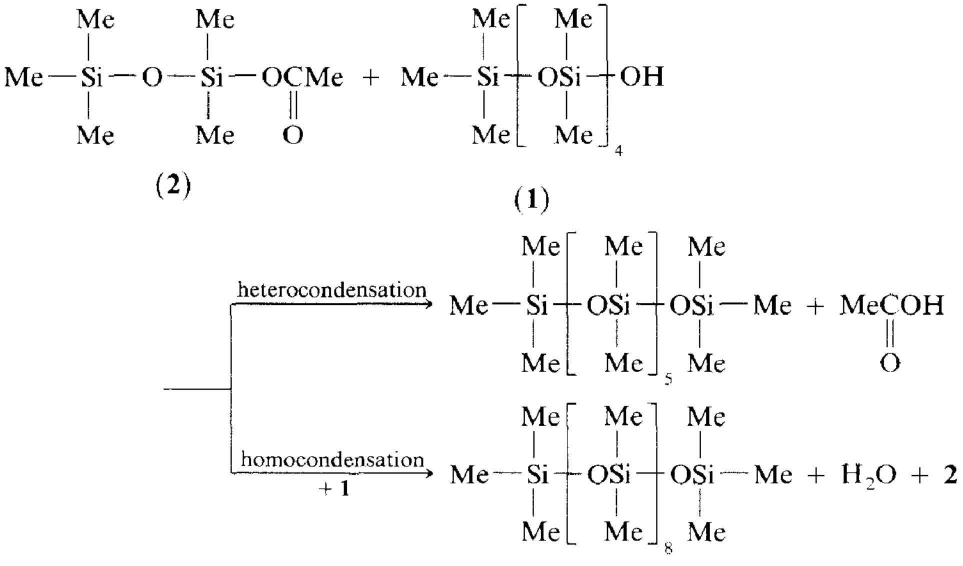
tetrahedral silicon cation intermediate postulated for analogous silanolysis of silyl chlorides [1] is less likely to operate in this system.

Results and discussion

The selectivity of the process

The model reactants used for studies of the heterocondensation of silanols with acetoxysilane end groups were undecamethylpentasiloxane-1-ol (**1**) and 1-acetoxypentamethyldisiloxane (**2**). The reaction mainly took the course shown in eq. 1, but the hetero- and homo-condensation were accompanied by processes involving disproportionation and acetylation of **1** and hydrolysis of **2**, so that other oligomeric products also appeared.



(1)

The process is not selective when the catalysis is by a protonic acid such as CF_3SO_3H, the heterocondensation product comprising only ca. one-third of all the oligomeric products (Table 1). The product composition indicates that there is extensive homocondensation, hydrolysis of the acetoxyl group, and disproportionation of the oligosiloxanol. In contrast, the reaction in the presence of amines proved to be highly selective towards the heterocondensation.

Condensation in the presence of triethylamine

The mechanism of catalytic action of triethylamine in condensation of oligosiloxanol with chlorooligosiloxane was shown to be quite different from that for the highly nucleophilic heterocycles pyridine, 4-dimethylaminopyridine, and imidazole [1]. Since initial results indicated that such behaviour might apply also to the present system, studies analogous to those described in ref. 1 were performed for the condensation of **1** with **2** catalysed by Et_3N. Triethylamine also acts as an acceptor of the acid released during the reaction, and so it was used in a relatively high concentration. It must be emphasized, however, that when traces of water and acid were removed, no reaction occurred without addition of triethylamine, clearly indicating that it is a catalyst.

Table 1

The selectivity of the heterocondensation of model $CH_3C(O)OSi\equiv$ and $HO\text{–}Si\equiv$ oligosiloxanes **2** and **1**, respectively in CH_2Cl_2 at 25 °C [a]

Catalyst	Initial catalyst concentration in mol dm^{-3}	Relative molar conversion of **2** per 1 mol of converted **1**	Yield of products as mol% of the converted oligomer **1**		
			Hetero-condensation	Homo-condensation	Others (involving disproportion or end group exchange
CF_3SO_3H	1.00×10^{-3}	0.95	35.5	32.0	32.5
Et_3N	0.200	1.0	95	0	5
Et_3N + DMAP	0.200 + 0.020	1.0	95	0	5

[a] Initial concentrations $[\mathbf{1}]_0$ and $[\mathbf{2}]_0$ were 0.200 mol dm^{-3}. The reaction was quenched after 80–90% of **1** had disappeared.

The progress of the heterocondensation of **1** and **2** was monitored by removing samples and subjecting them to GLC analysis. A series of runs at various initial concentrations of one component were performed with the initial concentrations of the two remaining components kept constant. The results were rather similar to those for the $\equiv SiCl + \equiv SiOH$ condensation [1].

The initial rate varied linearly with the initial concentration of the $\equiv SiOC(O)CH_3$ substrate, but plots of the initial rate against the variable Et_3N and $\equiv SiOH$ substrate initial concentration gave identical curves. The initial rate tended to level off with an increase of the concentration of **1** or Et_3N (Fig. 1). Such behaviour can be attributed to the formation of 1/1 hydrogen bonded complex between **1** and

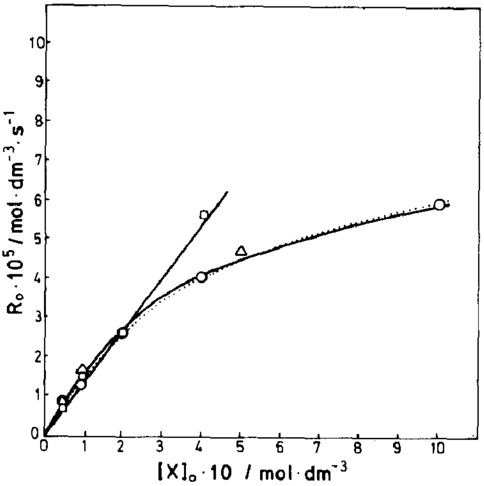
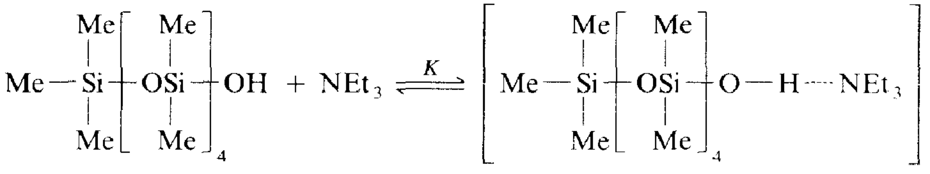


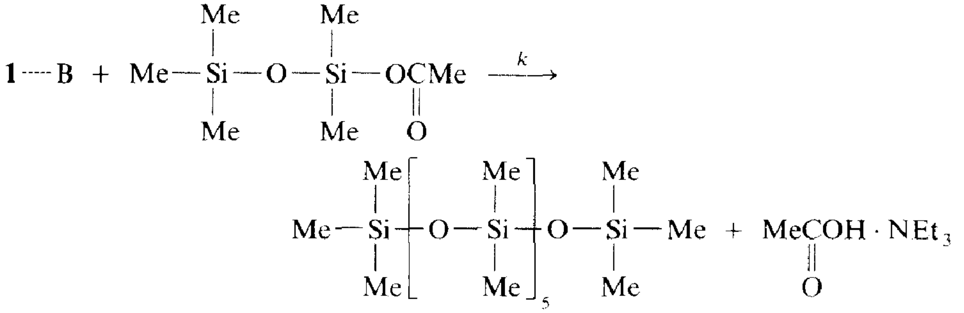
Fig. 1. Plots of the initial rate, R_0, for the condensation of undecamethylpentasiloxane-1-ol (**1**) with 1-acetoxypentamethyldisiloxane (**2**) in the presence of Et_3N in CH_2Cl_2 at 29 °C against the initial concentrations of: triethylamine ○———○ ($[\mathbf{1}]_0 = [\mathbf{2}]_0 = 0.200$ mol dm^{-3}); *1* △———△ ($[Et_3N]_0 = [\mathbf{2}]_0 = 0.200$ mol dm^{-3}); *2* □———□ ($[Et_3N]_0 = [\mathbf{1}]_0 = 0.200$ mol dm^3). The continuous line represents the least square line for all the experimental points for the series with variable $[Et_3N]_0$ and $[SiOH]_0$. The dotted line is the curve produced for operation *2* with K 4.4 mol^{-1} dm^3 and k 1.95×10^{-3} mol^{-1} dm^3 s^{-1}.

Et_3N in an initial fast reversible step, with the complex then treated with **2** in the rate-limiting step (eq. 2).



$$\mathrm{Me{-}\underset{Me}{\overset{Me}{Si}}{-}\left[O\underset{Me}{\overset{Me}{Si}}\right]_4{-}OH + NEt_3 \xrightleftharpoons{K} \left[Me{-}\underset{Me}{\overset{Me}{Si}}{-}\left[O\underset{Me}{\overset{Me}{Si}}\right]_4{-}O{-}H\cdots NEt_3\right]}$$

(**1** ···· B)



$$\mathbf{1}\cdots\mathrm{B} + \mathrm{Me{-}\underset{Me}{\overset{Me}{Si}}{-}O{-}\underset{Me}{\overset{Me}{Si}}{-}O\underset{\|}{C}Me} \xrightarrow{k}$$

$$\mathrm{Me{-}\underset{Me}{\overset{Me}{Si}}{-}\left[O{-}\underset{Me}{\overset{Me}{Si}}\right]_5{-}O{-}\underset{Me}{\overset{Me}{Si}}{-}Me + Me\underset{\underset{O}{\|}}{C}OH \cdot NEt_3} \quad (2)$$

The equilibrium constant for the formation of the Et_3N-**1** hydrogen bonded complex in CH_2Cl_2 was assumed to have the same value ($K = 4.4$, 25 °C) as that for the system $Et_3N/Me_3SiOSiMe_2OH$ previously determined in this solvent [1]. The concentration of the complex was calculated for all experimental points and a plot of the initial rate against this concentration was found to be linear (Fig. 2), indicating that the complex is the actual reactant in this reaction. The rate constant for the rate-limiting step was found from the slope of the line of Fig. 2 to be k

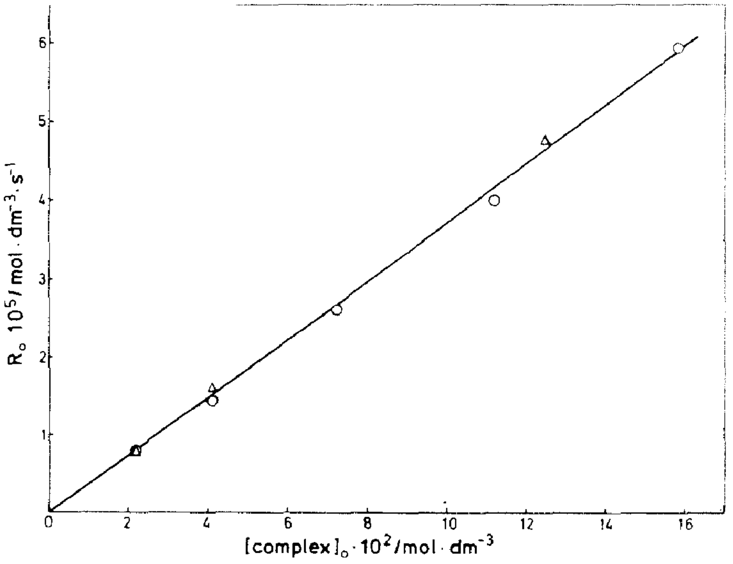


Fig. 2. Plot of the initial rate, R_0, against the initial concentration of complex **1**·NEt_3 for the condensation of **1** with **2** in methylene chloride at 25 °C in the presence of triethylamine. For the meaning of △, ○ see the caption to Fig. 1.

1.95×10^{-3} dm^3 mol^{-1} s^{-1} (25 °C). Thus the triethylamine is acting as a Brönsted base, promoting the reaction by enhancing the nucleophilicity of the silanol substrate.

Condensation in the presence of a triethylamine-nucleophile system

A series of condensations of **1** with **2** were performed for an equivalent concentration of Et_3N but with various catalytic amounts of 4-*N*,*N*-dimethylaminopyridine (DMAP) (Fig. 3).

As was observed for the condensation of oligosiloxanol with chlorooligosiloxane [1], and also for some similar systems [8–10], DMAP and some other *N*-heterocycles are much more effective catalysts than Et_3N (Table 2). However, in the present system the results for two component catalysts cannot be interpreted by neglecting the reaction involving catalysis by Et_3N, the contribution of which may be significant. The straight line representing the dependence of the initial rate on the

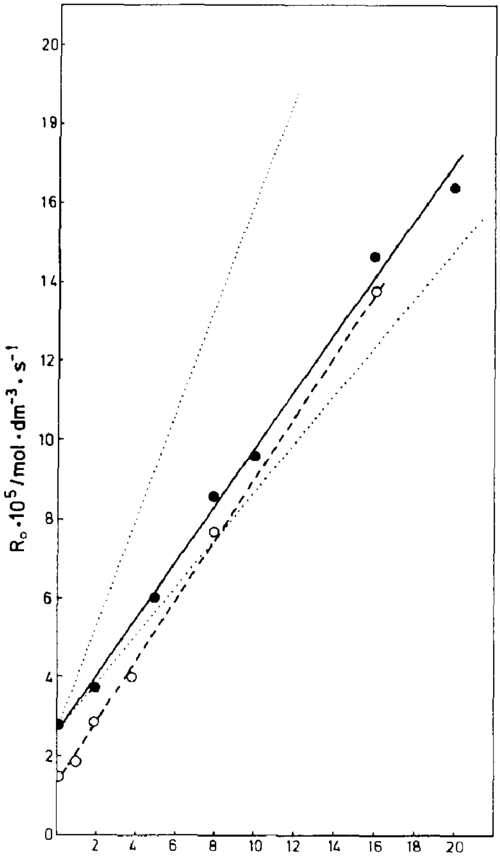


Fig. 3. Plots of the initial rate of the condensation of **1** with **2** in the presence of triethylamine against the concentration of DMAP in methylene chloride at 25 ° C, ○———○ $[Et_3N]_0$ 0.100 mol dm^{-3}, $[\mathbf{1}]_0 = [\mathbf{2}]_0 = 0.200$ mol dm^{-3}; ●———● $[Et_3N]_0 = [1]_0 = [2]_0 = 0.200$ mol dm^{-3}

Dotted lines refer to limiting cases for $[Et_3N]_0 = 0.200$ mol dm^{-3} on the assumption (upper line) that the **1**·NEt_3 complex is the only reactive form of **1** in the reaction catalyzed with DMAP and on the assumption (lower line) that the reaction proceeded only with uncomplexed **1** it being assumed also that in both these cases the dependence for $[Et_3N]_0$ 0.100 mol dm^{-3} is that observed, shown by the dashed line.

Table 2

Comparison of catalytic activities of organic basis in the heterocondensation of ≡SiX with ≡SiOH in CH_2Cl_2 at 25 °C [a]

Base	pK_B	≡SiAc + HOSi≡		≡SiClHOSi≡	
		R_0 (mol/dm^3 s)	$\frac{R_0}{R_0(Et_3N)}$	R_0 (mol/dm^3 s)	$\frac{R_0}{R_0(Et_3N)}$
Et_3N	3.30	2.8×10^{-5}	1	7.2×10^{-6}	1
Pyridine	8.85	2.4×10^{-6}	0.086	4.6×10^{-4}	64
DMAP	4.30	1.5×10^{-3}	54	2.3×10^{-2}	3200
Imine	6.97	5.8×10^{-4}	21	9.6×10^{-3}	1330
NMI	7.10	6.4×10^{-4}	25	6.7×10^{-3}	930
HMPA		1.1×10^{-4}	4	2.9×10^{-4}	40

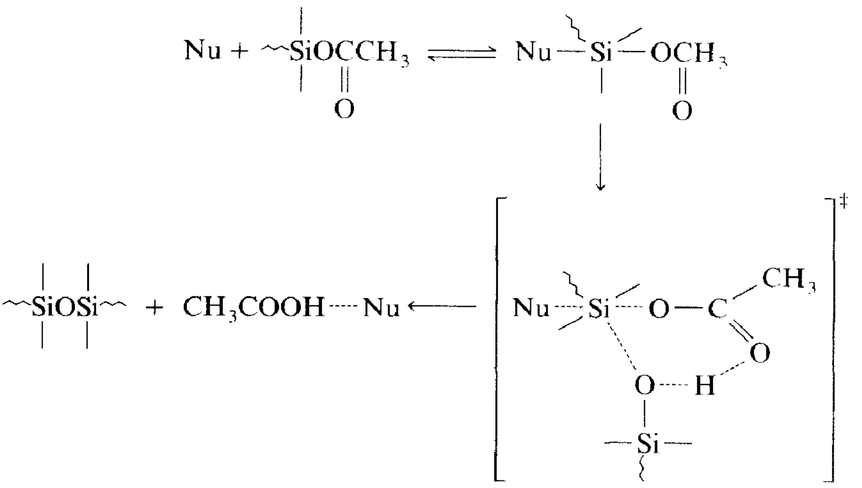
[a] Initial concentrations: $[SiX]_0 = [catalyst]_0 = 0.200$ mol dm^{-3}

nucleophile concentration crosses the ordinate at the value corresponding to the initial rate of the base-catalysed process. Such a dependence is indicative of a competition between two reactions, one catalysed by Et_3N and the other by DMAP, according to eq. 3.

$$R_0 = \frac{-d[\mathbf{1}]}{dt} = \frac{-d[\mathbf{2}]}{dt} = k_2 \cdot [\mathrm{DMAP}] \cdot [\mathbf{1}] \cdot [\mathbf{2}] + k_1 \cdot [\equiv \mathrm{SiOH} \cdots \mathrm{Et_3N}] \cdot [\mathbf{2}] \quad (3)$$

The intersection of the line with the ordinate corresponds to the rate of the condensation catalyzed by triethylamine, and the catalytic constant for the reaction promoted by DMAP can be calculated from the slope.

Similar experiments were performed for some other catalysts. Comparison of the effectiveness of various catalysts used (Table 2) indicates that nitrogen heterocycles and hexamethylphosphorotriamide must act as a nucleophile interacting with silyl acetate. Despite the similarities in kinetics features, the mechanism of the nucleophilic catalysis in this system may be somewhat different from that for the silanol/silyl chloride condensation [1]. Acetate ion is a much poorer leaving group than chloride ion, and so complete ionisation of the silyl acetate under the action of an uncharged nucleophile seems unlikely. Formation of a molecular complex between the catalyst and the acetoxysilane is more likely. This complex could react with silanol through a cyclic transition state involving extended coordination at silicon, as in eq. 4.



(4)

The intermediacy of hypervalent silicon species in nucleophile-catalyzed substitution at a silicon centre has been discussed by Corriu et al. [11–13], and strong evidence was offered in favour of the involvement of silicon species of high coordination numbers.

Examination of the data presented in Table 2 indicates that the nucleophilic catalysis is not as effective in this system as it is in the heterocondensation involving the chloride substrate. The reaction catalyzed by pyridine in the present system is slower than that in the presence of triethylamine under the same conditions, although pyridine was clearly more effective than Et_3N in the heterocondensation with the chloride substrate. DMAP increases the specific rate of the chloride condensation reaction more than 10^3 times as effectively as Et_3N, while the corresponding factor for the acetoxy-condensation is $< 10^2$.

Since Et_3N promotes the reaction by enhancement of nucleophilicity of the silanol while DMAP activates the silyl-acetate substrate by facilitating the departure of the leaving group, a synchronous action of these catalysts in a push-pull type mechanism is feasible, but the results of experiments performed at two different initial concentrations of Et_3N (Fig. 3) rules out this possibility. If it did operate the slope should increase with increasing Et_3N initial concentration (dotted line a), whereas there was in fact a slight fall in the slope. This fall can be attributed to the lowered activity of the Et_3N–silanol hydrogen bonded complex compared with that of the free silanol species in the reaction promoted by DMAP. It is noteworthy that the linearity of the plot also rules out the participation of DMAP in the reaction catalyzed by Et_3N.

Experimental

Methylene chloride and the catalysts triethylamine, pyridine, imidazole, 4-*N*,*N*-dimethylaminopyridine (DMAP), hexamethylphsophoroamide (HMPA), and trifluoromethanesulphonic acid, were all purified as described previously [1]. 1,1,3,3,5,5,7,7,9,9,9-Undecamethylpentasiloxane-1-ol (**1**) was prepared as previously described [14].

1-Acetoxy-1,1,3,3,3-pentamethyldisiloxane (**2**). A mixture of 1-chloropentamethyldisiloxane (36.5 g, 0.2 mol) and acetic anhydride (20.4 g, 0.2 mol) was kept at the reflux temperature as acetyl chloride was distilled off. After 5 h 13.5 ml (ca. 95%) of acetyl chloride had been collected. Distillation gave 40 g of the crude product, and fractional distillation through spinning band column gave 37 g (90% yield) of pure **2**, b.p. 145 °C.

The purities of substrates and catalysts were carefuly checked by GLC.

The kinetic investigations were carried out as described for the condensation of oligosiloxanes with silanol and silyl chloride end groups [1].

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