

Kinetics and mechanism of oligosiloxanol condensation and oligosiloxane rearrangement catalysed with model phosphonitrile chloride catalysts

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Abstract

The condensation kinetics of 1,1,3,3,3-pentamethyldisiloxanol (MDH) in *n*-heptane solution were compared for two types of phosphonitrilic catalyst, hexachloro-1 λ -diphosphaza-1-enium hexachloroantimonate salt, $[\text{Cl}_3\text{PNP}(\text{Cl}_3)]^+[\text{SbCl}_6]^-$, **1**, and *P*-trichloro-*N*-dichlorophosphoryle phosphazene, $[\text{Cl}_3\text{PNP}(\text{O})\text{Cl}_2]$, **2**. The kinetic law of reaction is not changed when **1** is replaced by **2**. The process is selective leading to linear decamethyltetrasiloxane (MD_2M , where D denotes the dimethylsiloxane unit, and M denotes the trimethylsiloxane unit) as almost the exclusive primary product. Other oligomers of the MD_nM series are formed as a result of the MD_2M rearrangement. The MD_2M rearrangement was studied in separate experiments in the absence of the siloxanol and water. Both catalysts **1** and **2** gave similar rate-concentration behaviour. Some of the kinetic features of the process resemble those of chain reactions and mechanisms of the MDH condensation, and the MD_2M rearrangement are discussed.

Keywords: Hexachlorodiphosphazanium ion; Polysiloxanes; Silanol polycondensation; Siloxane rearrangement; Phosphonitrile chlorides; Phosphazene

1. Introduction

Oligophosphazanium salts of general formula $[\text{Cl}_3\text{P}-(\text{N}=\text{PCl}_2)_n\text{Cl}]^+\text{X}^-$ where X is Cl or a complex ion, such as PCl_6^- , SbCl_6^- , AlCl_4^- and others, are well known as very efficient catalysts of silanol polycondensation and rearrangement of linear polysiloxanes [1–16]. Usually, mixtures of oligohomologues of these salts are used to condense low molecular weight oligosiloxanediols into a high molecular weight linear polymer. The advantage of using these catalysts is that the product of the polycondensation does not contain cyclic oligosiloxanes. These phosphonitrile chloride oligomers also promote redistribution of linear polysiloxanes without formation of a significant amount of cyclic species.

According to the recent patent literature [17] the products of reactions of oligophosphazanium salts with protic additives lead to catalysts which are also efficient silanol condensation and rearrangement catalysts. Another class of compounds which are claimed to be

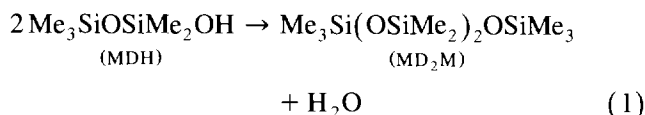
catalysts in these processes are oligomers of neutral phosphoryl phosphazenes of general formula $\text{Cl}[\text{P}(\text{Cl})_2=\text{N}]_n\text{P}(\text{O})\text{Cl}_2$, and $\text{HO}[\text{P}(\text{Cl}_2)=\text{N}]_n\text{P}(\text{O})\text{Cl}_2$, $n = 1, 2, \dots$ [16–18]. The viscosity change during the polycondensation of oligodimethylsiloxanols in the presence of various types of phosphazene-derived catalysts has recently been studied by Hager and Weis [16]. These authors showed that the neutral phosphorylphosphazenes are even more effective in promoting this polycondensation.

Although the silanol condensation and the siloxane rearrangement in the presence of phosphazene derivatives are the subject of many patents the mechanism of these catalytic processes has not been recognized. This scarcity of knowledge on catalysis by oligophosphazanium ions in polysiloxane chemistry prompted us to perform kinetic studies of the title reactions using selected model substrates and catalysts. The mechanisms of catalysis by oligophosphazanium salts and by phosphoryl oligophosphazenes may be closely related. The phosphoryl oligophosphazenes are formed as products of the interaction of corresponding oligophosphazanium salts with water [19] and with silanols [16,20]. Thus,

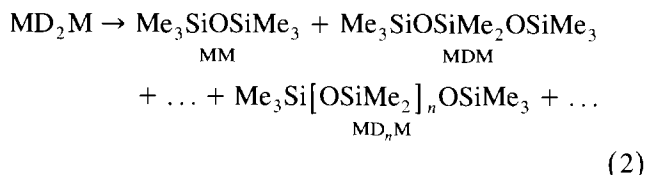
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they may appear early in the silanol polycondensation system when an oligophosphazanium ion is used as catalyst. We have therefore performed a comparative study of the kinetics of condensation of a model siloxanol in the presence of an oligophosphazanium ion and corresponding phosphorylphosphazene to throw some light on the mechanism of this polycondensation.

1,1,3,3,3-Pentamethyldisiloxane-1-ol (MDH) was used as the model substrate in this polycondensation study since it is the simplest stable oligosiloxanol and its condensation leads to only one product according to Eq. (1).



MD₂M, where D denotes the dimethylsiloxane unit, and M denotes the trimethylsiloxane unit, rearrangement (redistribution) according to Eq. (2) is the consecutive reaction



The redistribution was studied in a separate system using the same catalysts and solvent as those used in the condensation studies, but the system did not contain silanol and consequently there was no water present.

Well-defined single diphosphorus species were used as the oligophosphazene catalysts. Thus, hexachlorodiphosphazanium hexachloroantimonate $[\text{Cl}_3\text{PNPCl}_3]^+\text{SbCl}_6^-$, **1**, and product of its hydrolysis *P*-trichloro-*N*-dichlorophosphorylphosphazene $\text{Cl}_3\text{P}=\text{N}-\text{P}(\text{O})\text{Cl}_2$, **2**, were selected to promote both the MDH condensation and the MD₂M redistribution.

Dimers are the simplest oligophosphazanium ions and some of their salts are well known and well characterized chemical compounds [21–30]. Thus, **1** can be easily synthesized, isolated and purified. These salts are soluble in some chlorinated hydrocarbons, although their solubility is limited. Compound **2** is a well known intermediate in dichlorophosphazene polymer chemistry [31]. It is soluble in hydrocarbons and is stable in a dry solution [32].

2. Results and discussion

2.1. Kinetics of condensation of 1,1,3,3,3-pentamethyldisiloxane-1-ol (MDH)

Reactions were performed in *n*-heptane containing small amounts (up to 2 wt.%) of 1,1,2,2-tetrachloro-

ethane in which the catalyst stock solutions were prepared and introduced to the reaction system. Kinetics were investigated by sampling the reaction mixture and determining the substrate MDH and product MD₂M concentrations by gas-chromatography. Reactions were followed to a conversion of 60–98%. In the first stage of the process MD₂M was formed as almost the sole product of the reaction for both catalysts **1** and **2** (an example is shown in Fig. 1). In particular, oligomers of the MD_nH series were not produced, thus, disproportionation of MDH, which had been observed in many other siloxanol polycondensations, did not occur to any significant extent. Substantial amounts of the MD_nM oligohomologue series only appeared at a high substrate conversion and were formed as a result of the consecutive redistribution reaction (Eq. (2)).

The reaction proceeded according to the second-order kinetic law for the both catalysts **1** and **2** (Figs. 1 and 2). The reaction led to almost complete conversion of MDH, which was in agreement with earlier observations that the equilibrium of silanol condensation in aprotic media lies well towards products [33,34]. Thus, in the kinetic analysis the reaction was considered to be irreversible. Only when very low concentrations of catalyst **1** were applied did deviations from second order occur. The condensation reaction slowed down at higher conversions, presumably as a result of the irreversible loss on decomposition of an active form of the catalyst.

Considerable amounts of water were released during the reaction and a dispersed water phase appeared in the

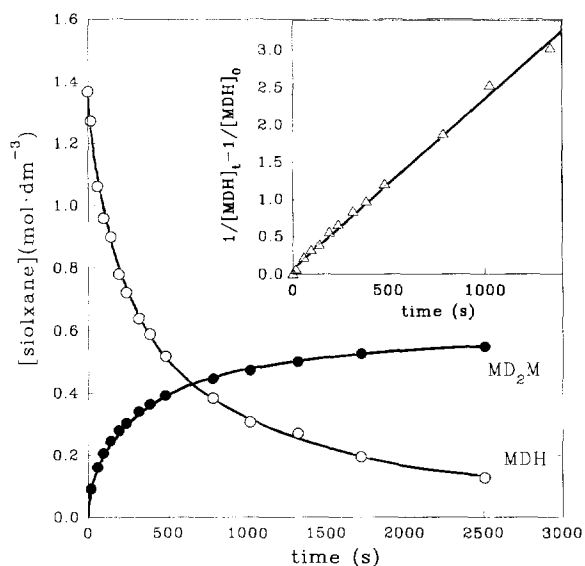


Fig. 1. Condensation of 1,1,3,3,3-pentamethyldisiloxane-1-ol, MDH, in *n*-heptane at 25°C in the presence of hexachlorodiphosphazanium hexachloroantimonate, **1**. $[\text{MDH}]_0 = 1.50 \text{ mol dm}^{-3}$, $[\text{Cl}_3\text{PNPCl}_3]^+\text{SbCl}_6^-]_0 = 1.03 \times 10^{-3} \text{ mol dm}^{-3}$ substrate conversion–time and product formation–time dependences: ○ MDH; ● MD₂M. The second-order plot for the substrate conversion is placed in the upper right part of the figure.

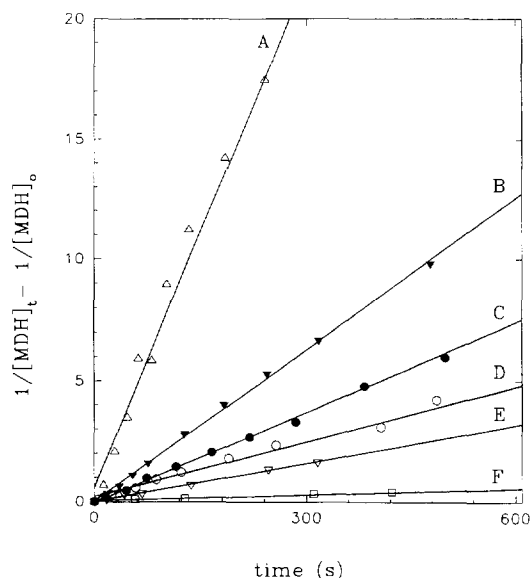


Fig. 2. Second-order plot for the condensation of MDH in *n*-heptane in the presence of **2**, at 25°C. Initial concentrations (mol dm^{-3}) of MDH and **2** respectively were: (A) 0.23, 1.1×10^{-3} ; (B) 0.9, 1.1×10^{-3} (55°C); (C) 0.5, 1.1×10^{-3} ; (D) 0.9, 1.3×10^{-3} ; (E) 0.9, 1.1×10^{-3} ; (F) 1.9, 1.1×10^{-3} .

early stage of the process. Thus, a stationary water concentration in the organic phase is established very soon after the beginning of the reaction.

A series of condensations catalysed with **1** was performed at variable initial substrate concentrations. Results presented in Fig. 3 indicate that the specific rate decreases with increasing substrate concentration and the slope of the second-order rate constant vs. initial MDH concentration in a double logarithmic plot is -2 , which corresponds to the apparent external order in

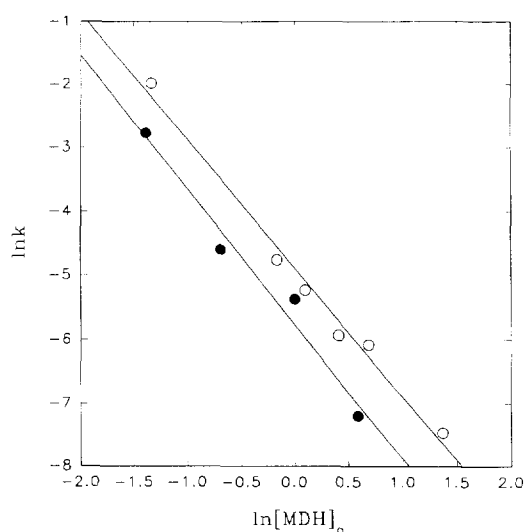


Fig. 3. Dependence of \ln of the second-order rate constant on the \ln of the initial concentration of MDH for the condensation of MDH in the presence of **1** (O) and **2** (●); temperature 25°C. Catalyst concentration adjusted to $1.00 \times 10^{-3} \text{ mol dm}^{-3}$.

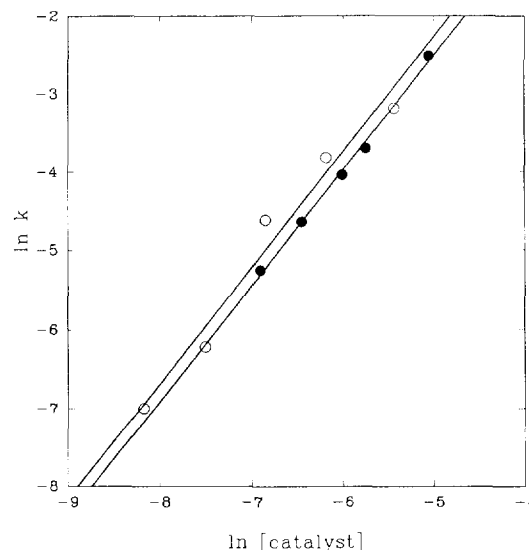


Fig. 4. Dependence of \ln of the second-order rate constant on the \ln of the concentration of catalyst for the condensation of MDH in the presence of: **1** (O), $[\text{MDH}]_0 = 1.00 \text{ mol dm}^{-3}$; **2** (●), 25°C, $[\text{MDH}]_0 = 1.00 \text{ mol dm}^{-3}$.

MDH equal to zero. An analogous series of experiments was performed for the MDH condensation catalysed by **2** and similar results were obtained (Fig. 3).

A series of runs was also performed at different catalyst concentrations. The catalytic activity of **1** and **2** are compared in Fig. 4. Both catalysts displayed a similar kinetic behaviour. Both catalysts gave the same slope of 1.5 in a double logarithmic plot of the rate-concentration dependence (Fig. 4).

Results of experiments performed at different temperatures allowed the estimation of the activation energies for both catalysts (Table 1), which are similar. Some MDH condensation experiments catalysed by **1** were also performed in methylene chloride (dielectric constant $\epsilon = 9$). The reaction in this solvent proceeded faster than that in *n*-heptane (dielectric constant $\epsilon = 2$) by a factor of about three. Thus, by using a solvent with higher dielectric constant the rate of condensation is increased but the effect is not dramatic.

Table 1

Comparison of kinetic features of the condensation of MDH in the presence of two catalysts: $(\text{Cl}_3\text{PNPCl}_3)^-\text{SbCl}_6^-$ (**1**) and $\text{Cl}_3\text{PNP}(\text{O})\text{Cl}_2$ (**2**)

Kinetic feature	Catalyst	
	1	2
Internal order in substrate	2	2
Apparent external order in substrate	0.0	-0.1
Apparent order in catalyst	1.5	1.5
Activation energy E_A (kcal mol^{-1})	12.9	9.1
Second-order rate constant k_{11} ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) ^a	9.9×10^{-3}	5.2×10^{-3}

^a 25°C, $[\text{MDH}]_0 = 1.00 \text{ mol dm}^{-3}$, $[\text{cat}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$.

Table 2
Redistribution of MD₂M catalysed by **1** in *n*-heptane, [MD₂M] = 0.70 mol dm⁻³

No	1×10^4 (mol dm ⁻³)	Temperature (°C)	[H ₂ O] ₀ × 10 ⁴ (mol dm ⁻³)	$k_1 \times 10^4$ (s ⁻¹)	Induction period (s)	E_A (kcal mol ⁻¹)
1	1.01	60	0	1.21	2500	
2	3.10	60	0	5.0	150	
3	10.4 ^a	60	0	15.0	200	
4	3.10	60	3.0 ^b	8.5	none	
5	3.10	60	3.0 ^c	5.5	none	
6	3.10	60	6.0 ^b	7.1	none	
7	3.10	40	6.0 ^b	2.5	none	8
8	3.10	80	6.0 ^b	9.0	none	

^a In the beginning of the process part of the catalyst formed a separate phase. The slope was measured within the stage of the reaction when the catalyst was fully dissolved.

^b Water was premixed with the catalyst stock solution, which was subsequently used after a short time (about 15 min) to catalyse the reaction.

^c Water was premixed with the catalyst stock solution, which was used to catalyse the reaction after standing for 2 days.

Formation of the rearrangement product MD₃M in the MDH condensation system was a slow process. The estimated rate of the redistribution reaction was lower than that of condensation by about two orders of magnitudes (40 times).

Kinetic features of the condensation reaction catalysed by **1** and **2** are summarized in Table 1. There is a striking similarity between processes catalysed by these quite different catalysts. Both show the same kinetic law, i.e. the same internal order in substrate and the same external orders with respect to MDH and to catalyst. The reaction catalysed by the phosphazanium salt is less than twice as fast as the reaction catalysed by the phosphoryl phosphazene species under the same conditions.

2.2. Kinetics of redistribution of linear decamethyltetrasiloxane, MD₂M

The reaction was performed in an analogous way to the MDH condensation, i.e. in *n*-heptane containing a small amount of (Cl₂CH)₂. The conversion was followed in the same way by g.c. analysis. Both catalysts **1** and **2** were explored. The redistribution led to an equilibrium mixture of the homologue series of MD_{*n*}M, *n* = 0, 1, 2, ... and of D_{*m*}, *m* = 4, 5, ... The formation of

cyclic oligomers was considerably delayed in relation to the formation of linear species. Thus, the kinetic analysis was based on the assumption that the redistribution leads exclusively to the equilibrium between linear species, thus neglecting the formation of cyclic species. Indeed, this quasi-equilibrium concentration of MD_{*n*}M species was found to be similar to that calculated according to the Flory statistical treatment for equilibrium between MD_{*n*}M species.

The kinetics are further complicated for both the catalyst systems by an induction period. The substrate concentration–time dependences are S-shaped (see Fig. 5). Generally, the length of the induction period depends on the catalyst concentration and in some cases ([**1**] = 10⁻⁴ mol dm⁻³) reaches 2000–3000 s (Tables 2 and 3). However, at a higher catalyst concentration (3 × 10⁻⁴ mol dm⁻³), this period is relatively short (Fig. 5). The length of the induction period seems to depend on the substrate concentration as well. It was not observed when the rearrangement catalysed with **2** was carried out in bulk (Table 3, entry 7).

In the stationary state of the process the reaction for both catalysts **1** and **2** proceeds according to first-order kinetics (Figs. 5–7). The addition of water to the reaction system had considerable impact on the rate and on the shape of the kinetic curves (Tables 2 and 3, Figs. 6

Table 3
Redistribution of MD₂M catalysed by **2** in *n*-heptane

No	[MD ₂ M] ₀ (mol dm ⁻³)	[2] ₀ × 10 ³ (mol dm ⁻³)	Temperature (°C)	[H ₂ O] ₀ (mol dm ⁻³)	$k_1 \times 10^3$ (s ⁻¹)	Induction period (s)	E_A (kcal mol ⁻¹)
1	0.69	2.09	25	0	1.23	300	
2	0.69	2.09	40	0	1.90	300	6.0
3	0.69	2.09	60	0	3.56	none	
4	0.69	2.09	40	6 × 10 ⁻³	2.88	none	
5	0.69	0.505	40	0	0.97	100	
6	0.69	0.101	40	0	0.14	2000	
7	2.41	2.06	40	0	3.33	none	

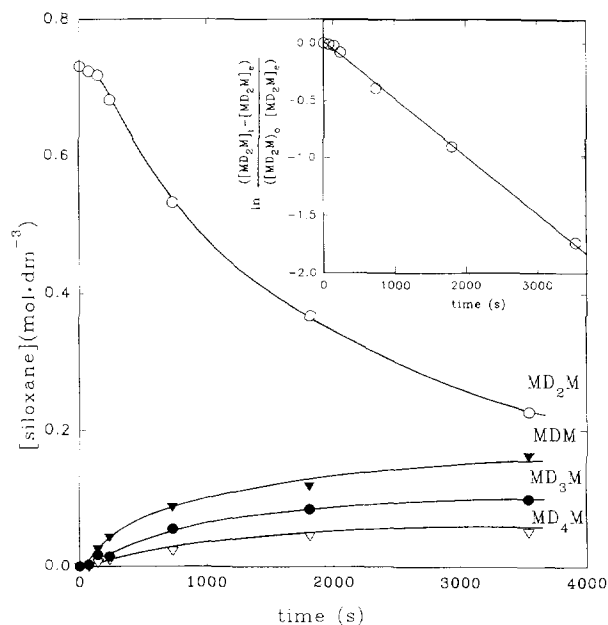


Fig. 5. Redistribution of MD₂M in *n*-heptane in the presence of **1** at 60°C with no additional water, [1] = 0.30 × 10⁻³ mol dm⁻³. Substrate conversion–time dependence and product formation–time dependences: ○, MD₂M; ▼, MDM; ●, MD₃M; ▽, MD₄M. The first-order plot for the MD₂M conversion is placed in the upper right part of the figure.

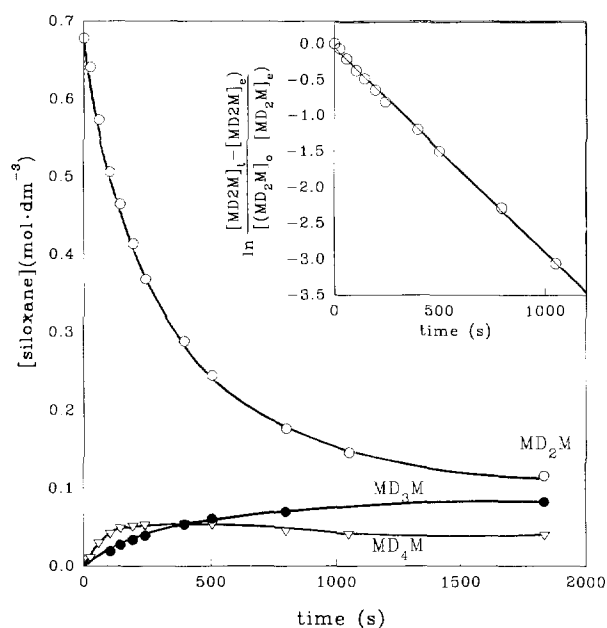


Fig. 7. Redistribution of MD₂M in *n*-heptane in the presence of **2** at 40°C with water premixed with the catalyst stock solution, [2] = 2.09 × 10⁻³ mol dm⁻³, [H₂O]₀ = 6 × 10⁻³ mol dm⁻³. Substrate conversion–time dependence and product formation–time dependences: ○, MD₂M; ●, MD₃M; ▽, MD₄M. In the upper right part of the figure is the first-order plot for the MD₂M conversion.

and 7). A small amount of water premixed with the stock solution of **1** for about 10–15 min prior to addition of the catalyst to the substrate solution increased

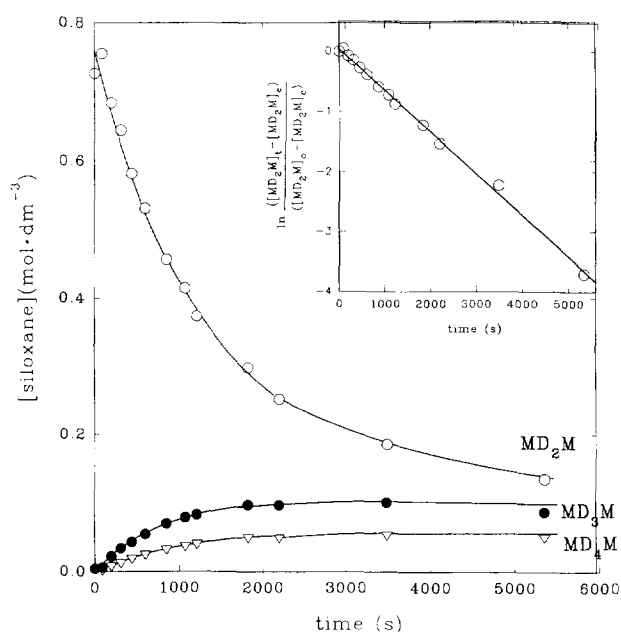
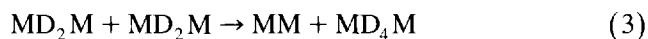


Fig. 6. Redistribution of MD₂M in *n*-heptane in the presence of **1** at 60°C with water premixed with the catalyst stock solution, [1] = 0.30 × 10⁻³ mol dm⁻³, [H₂O]₀ = 0.60 × 10⁻³ mol dm⁻³. Substrate conversion–time dependences and product formation–time dependences: ○, MD₂M; ●, MD₃M; ▽, MD₄M. In the upper right part of the figure is the first-order plot for the MD₂M conversion.

the reaction rate (Table 2, entry 4) by a factor of about two and suppressed the induction period (see also Fig. 6). Addition of a larger quantity of water to **1** (Table 2, entry 6) or premixing water 2 days before the reaction (Table 2, entry 5) also suppressed the induction period, although this had a smaller effect on the rate.

Formation characteristics of MD₃M and MD₄M during the MD₂M substrate conversion are dependent on the catalyst used. In the case of **1** oligomers are formed in parallel, while in the case of **2** MD₄M is initially formed in excess and its concentration passes a maximum, then decreases to achieve its equilibrium value (compare Figs. 5–7). Thus, the following reaction initially dominates:



The kinetic features of the MD₂M redistribution catalysed by **1** and **2** are compared in Table 4. Both catalysts give almost identical substrate concentration–time behaviour and addition of water has a similar influence on the activity of both catalysts. The rates of reactions promoted by **1** and **2** under the same conditions are very similar to each other.

2.3. Mechanisms of condensation and redistribution processes

The striking similarities between the two catalysts **1** and **2** (Tables 1 and 4) suggest that both involve the

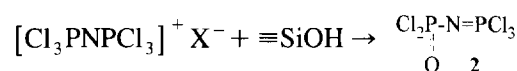
Table 4

Comparison of some kinetic features of the MD₂M rearrangement catalysed by two catalysts: (Cl₃PNPCl₃)⁺SbCl₆⁻ (**1**) and Cl₃PNP(O)Cl₂ (**2**)

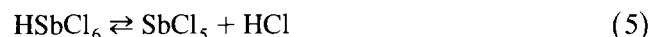
Kinetic feature	Catalyst	
	1	2
Internal kinetics	induction period first order	induction period first order
Order in catalyst	~ 1	~ 1
Effect of H ₂ O premixed with catalyst [H ₂ O]:[cat] = 2:1	acceleration suppression of induction period	acceleration suppression of induction period
First-order rate constant <i>k</i> ₁ (s ⁻¹) ^a	1.7 × 10 ⁻⁴	1.4 × 10 ⁻⁴
Activation energy <i>E</i> _A (kcal mol ⁻¹)	8	6.1
Product formation	MD ₃ M and MD ₄ M formed parallel	MD ₄ M is initially formed, later MD ₃ M

^a Temperature 40°C, [cat] = 1 × 10⁻⁴ mol dm⁻³, [MD₂M] = 0.7 mol dm⁻³.

same intermediates. It is known that interaction of water or silanol with **1** results in the cleavage of chlorine [16,20,21] giving **2** according to Eq. (4).



The reaction in Eq. (4) may involve the unstable Cl₃PNPCl₂(OSi≡)⁺ cation [20] which under the action of the second silanol molecule is transformed to **2** and siloxane. The reaction in Eq. (4) occurs immediately under the conditions of the silanol condensation process; thus, **1** is rapidly converted to **2** and HX in the very beginning of this process. HX being HSbCl₆ or its more complexed form is decomposed according to Eq. (5).



Compound **2** is partly protonated in the system, which explains the variation of the ³¹P NMR resonance of its phosphorus nuclei with changes in temperature and medium. The chemical shift of the -NPCl₃ moiety was shifted by 1.9 ppm towards higher field on changing temperature from -20°C to +25°C (Fig. 8(a-c)), while that of P(O)Cl₂ was only shifted by 0.4 ppm in the same direction.

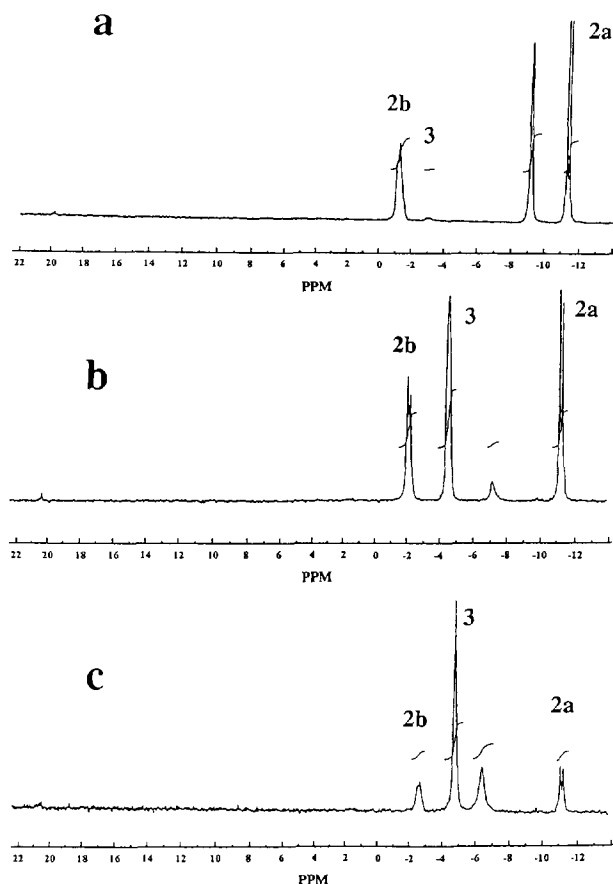
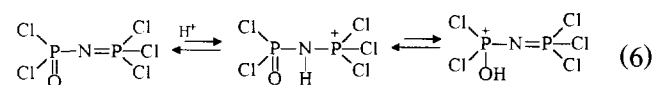
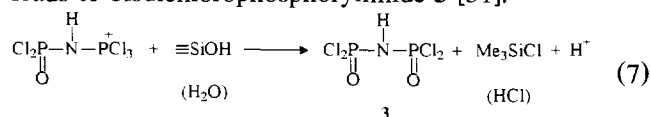


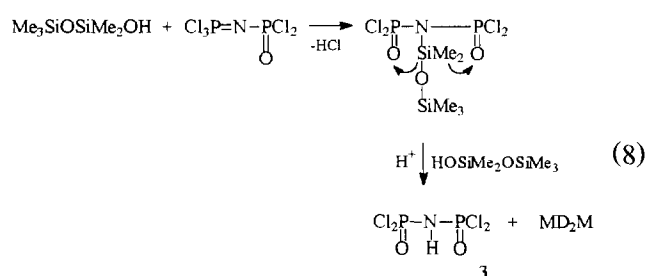
Fig. 8. ³¹P{¹H} NMR spectra of **2** + MDH mixture in Cl₂HC-CHCl₂, [2]₀ = 4.8 × 10⁻² mol dm⁻³, [MDH]₀ = 1.1 mol dm⁻³ prepared below -20°C. The spectra were taken (a) at -20°C, (b) after warming to 0°C, (c) after warming to +25°C. Marked are the signals of **2** (2a -N-P(O)Cl₂, 2b -N-PCl₃) and **3** (**3**).

The protonated form of **2** could thus undergo further reaction with silanol or water leading to further substitution of chloride, according to the reaction in Eq. (7) which is in agreement with the general mechanism of silanol condensation suggested by Hager and Weis [16]. Also, it has been shown that controlled hydrolysis of **2** leads to bisdichlorophosphorylimide **3** [31].



The reaction of **2** with MDH was studied by us by ^{31}P NMR. A large excess of MDH was introduced to the solution of **2** in 1,1,2,2-tetrachloroethane at -20°C and the ^{31}P NMR proton decoupled spectrum was immediately taken (Fig. 8(a)). The temperature was then raised in stages to 0°C and 25°C and the spectrum rerun after each stage (Fig. 8(b) and Fig. 8(c)). These spectra were compared with spectra of 1:1 mol/mol mixture of **2** with water taken at -20°C and $+25^\circ\text{C}$. The dominating signal in the spectrum of the reaction product of **2** with MDH at -5 ppm (25°C) (Fig. 8(c)) and -4.7 ppm (0°C) (Fig. 8(b)) is assigned to **3** and corresponds to the hydrolysis product of **2** with H_2O , at -4.5 ppm (25°C) and -4.3 ppm (0°C), (Fig. 9). A strong signal at -8.9 ppm is seen in the spectrum of **2** with MDH taken at -20°C (Fig. 8(a)) which dis-

appears on increasing the temperature, indicating that an intermediate is formed. We believe that the intermediate is *N*-silylated **3** or *O*-silylated **3** assuming fast migration of the silyl group. Thus, the reaction, which occurs during the NMR experiment, may take the following course:



The position of the signal for **3** is also sensitive to the medium and temperature and may be found in the range $+1$ to -8 ppm [31]. **3** may appear in various neutral protonated and anionic forms according to Eq. (9):

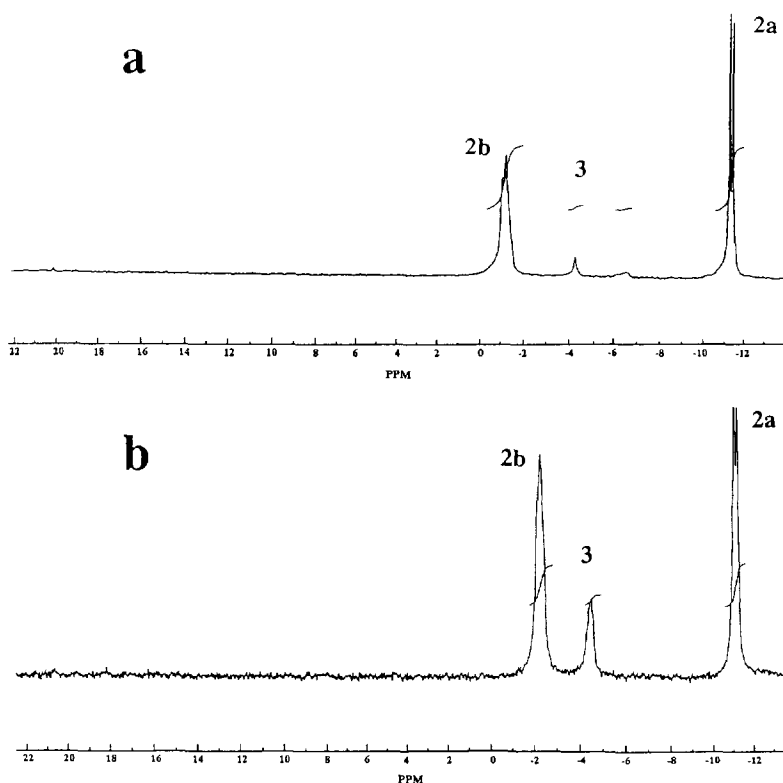
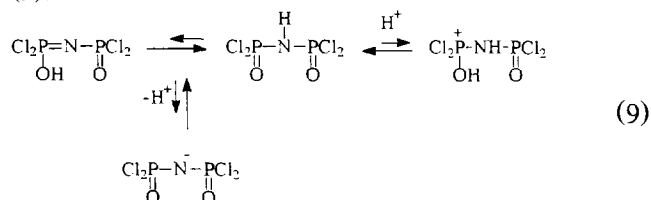


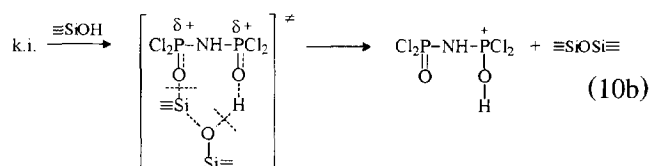
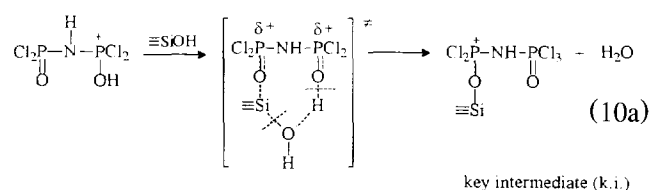
Fig. 9. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **2** + H_2O 1:1 molar mixture in $\text{Cl}_2\text{HC}-\text{CHCl}_2$, $[\mathbf{2}]_0 = 4.8 \times 10^{-2} \text{ mol dm}^{-3}$, prepared below -20°C . The spectra were taken (a) at -20°C , (b) after warming to $+25^\circ\text{C}$. Signals of **2** are marked by 2a [$-\text{N}-\text{P}(\text{O})\text{Cl}_2$] and 2b [$-\text{NPCl}_3$]; signals of **3** are marked by 3.

Since the transformations presented in Eq. (9) are very fast and lead to an equilibrium, only one ^{31}P NMR signal is observed. Thus, **3** in the reaction system has both electrophilic and nucleophilic centres and may serve as an important intermediate in the condensation of silanols and the rearrangement of siloxanes.

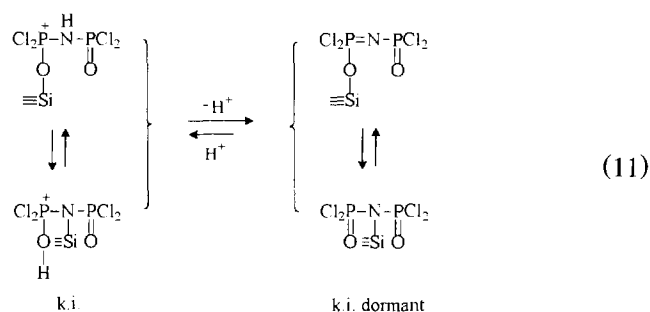
Further cleavage of chlorine in **3** is more difficult. Such a conclusion may be drawn from the analogy of the reaction of hexachlorodiphosphazanium ion with alcohol which predominantly led to substitution of two chlorine atoms and formation of a symmetrical product [20]. Substitution of subsequent chlorine was more difficult. Similarly, reaction of **2** with silanol or water leads to high yield of symmetrical product **3**. Further reaction of **3** with water or silanol leads to unstable diphosphorus products which decompose with the cleavage of the P–N–P bridge giving monophasic products [31] which are not very active condensation catalysts. This explains why the catalyst loses its activity in the condensation system after a long time, which was observed in experiments performed at low concentrations of **1**.

Studies of the effect of proton scavenger on the reaction of MDH catalysed with **1** has been made [35]. The addition of 2,6-di-*t*-butylpyridine to the reaction system in molar proportion of 0.3:1 catalyst was found to cause a dramatic decrease in the reaction rate. This observation indicates that a protonated species is the important reactive intermediate in this reaction. Protonated silyl ester of **3** (or its *N*-silyl isomer) could be this intermediate as its stationary concentration in the condensation system may be established at the beginning of the process. The proton-donating ability of the system is controlled not only by the HCl released in the process but also by phase equilibria which control the water concentration available for the reaction. This may lead to stationary concentrations of H^+ and, in consequence, to the simple second-order kinetics for the condensation. It should be noted that various silyl esters of **3** and their polyphosphazene homologues were claimed as catalysts of silanol condensation [18].

The condensation would occur as a result of the following steps (Eqs. (10a) and (10b)):



The second step of this mechanism corresponds to the second step of the reaction in Eq. (8) and the intermediate in the reaction in Eq. (8) detected by ^{31}P NMR is a dormant form of the key intermediate (Eq. (11)). The k.i. is submitted to fast proton exchange and it appears mostly in non-protonated form. It also undergoes silyl group migration (Eq. (11)); thus, its alternative form contains silicon bound to nitrogen. Consequently, an analogous pathway to that in Eqs. (10a) and (10b) involving *N*-silyl forms of the k.i. transition states may operate.



The role of protons in this mechanism is to convert the silyl ester of phosphorus or silyl amide of phosphorus structures into the corresponding phosphonium ion structures in which the propensity of the silyl group to react with a nucleophile is extremely high [20,36,37].

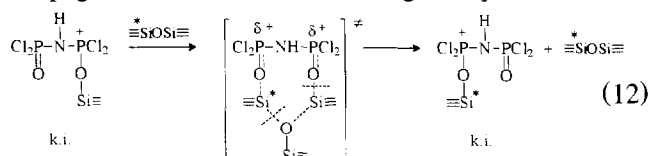
The observed kinetics are in agreement with this mechanism. The steady state concentration of the key intermediate in the silanol condensation system is relatively low compared to the initial concentrations of catalysts because it immediately reacts with water and silanol. Thus, the steady state k.i. concentration is proportional to the substrate concentration, which leads to second-order kinetics.

The strange dependence of the rate on the initial silanol concentration requires comment. Since k.i. is a protonated form of $\text{Cl}_2(\text{O})\text{P}-\text{N}=\text{P}(\text{OSi}\equiv)\text{Cl}_2$ its concentration depends upon the acidity of the medium. Introduction of silanol decreases the ability of acids present in the system to protonate **3** and the dormant form of k.i. This decreases the stationary concentration of the k.i. and decreases the rate of condensation. Moreover, increase in the silanol concentration enhances water concentration in the reaction phase which additionally decreases the stationary k.i. concentration.

¹ A mixture of oligohomologues of $[\text{Cl}_3\text{P}(\text{N}(\text{PCl}_2)_n\text{Cl})^+ \text{SbCl}_6^-]$ containing about 50% of **1** was used [3].

$[H^+]$ and $[3]$ are related to the initial concentration of catalyst. These relations are not straightforward, particularly for $[H^+]$, as a phase equilibrium is involved. Thus, the apparent order 1.5 with respect to catalyst observed for both **1** and **2** seems to be in agreement with the above mechanism.

Kinetic results of MD_2M redistribution are rationalized assuming a mechanism involving a similar k.i. Propagation would occur according to Eq. (12):



Since there is no water and silanol in the MD_2M redistribution system the dormant form of intermediate should be more stable. Indeed, after addition of 1:1 mixture of MD_2M and **1** at -20°C the ^{31}P NMR spectrum taken at this temperature shows a broad signal centred at -8.5ppm which could be assigned to a mixture of silylated **3** of general formula $[\text{Cl}_2(\text{O})\text{P}]_2\text{N}(\text{SiMe}_2\text{O})_n\text{SiMe}_3$, $n = 0, 1, 2$ (Fig. 10). The confirmation of this assignment could be the spectrum of **2** after the introduction of a large excess of hexamethyldisiloxane, MM, which transforms **2** into $[\text{Cl}_2(\text{O})\text{P}]_2\text{NSiMe}_3$ giving rise to the phosphorus resonance at -9.6ppm (Fig. 11).

The initiation of the redistribution is the formation of the k.i. In contrast with the condensation process, where the k.i. is formed relatively fast, the initiation of the redistribution is slow unless a small amount of a protic

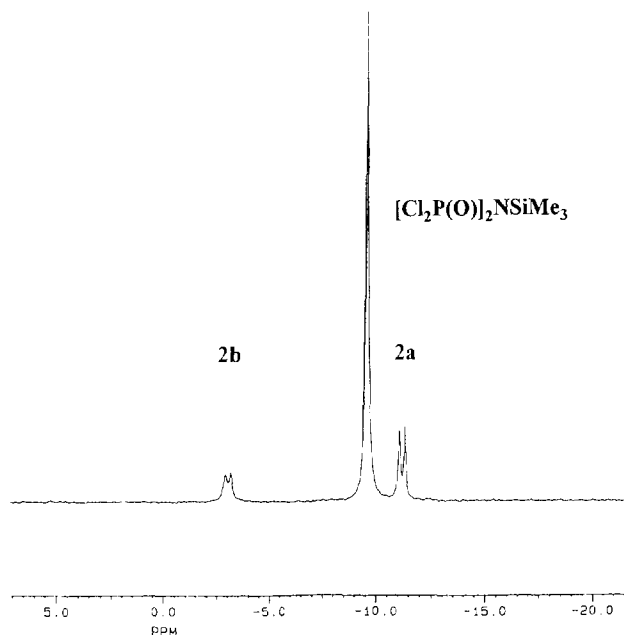


Fig. 11. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** + MM (hexamethyldisiloxane) 1:10 molar mixture in CH_2Cl_2 ; $+25^\circ\text{C}$, $[\mathbf{2}] = 0.5 \times 10^{-2} \text{ mol dm}^{-3}$.

species is introduced to the system. The reaction of siloxane with phosphazanium ion (Eq. (13a)) is analogous to that of ethoxysilane with the phosphazanium ion [20]. The reaction (Eq. (13a)) occurs slower compared with that of trimethylethoxysilane, but the silylated salt formed reacts relatively fast with any protic species being in the system, producing **2** and a strong protic acid (the reaction in Eq. (13b)). This acid catalyses the subsequent reaction of **2** with siloxane or a protic

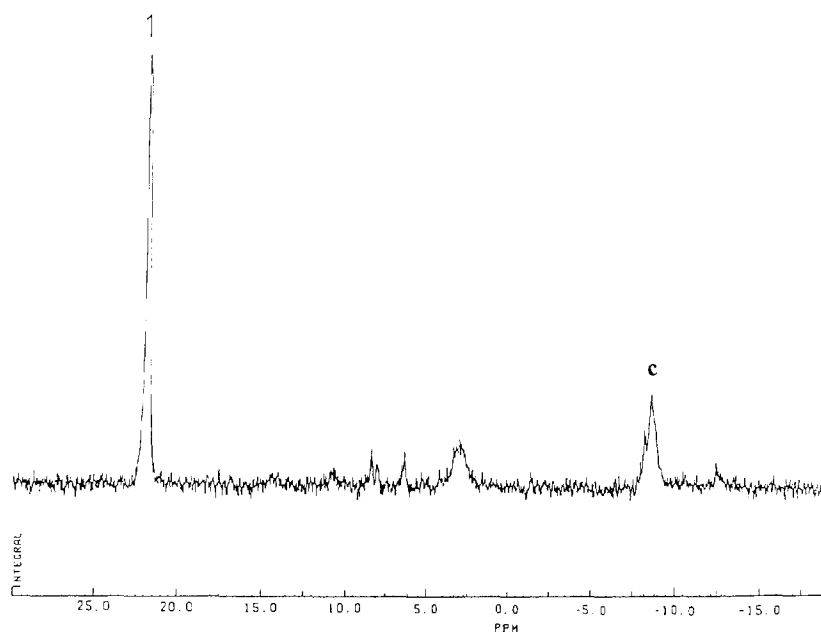
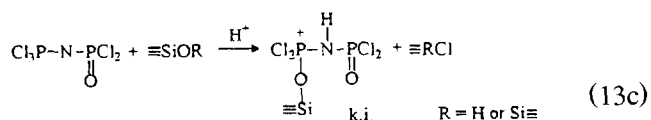
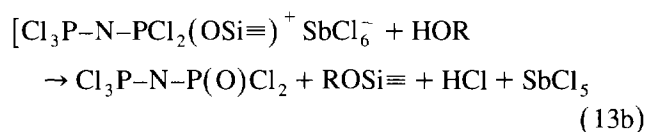
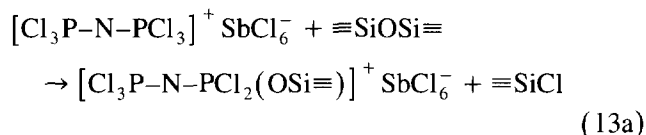


Fig. 10. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1** + MD_2M equimolar mixture ($[\mathbf{1}]_0 = 3.9 \times 10^{-2} \text{ mol dm}^{-3}$) in $\text{Cl}_2\text{HC}-\text{CHCl}_2$, temperature -20°C . Signal of **1** is marked by 1; signals believed to belong to $[\text{Cl}_2(\text{O})\text{P}]_2\text{N}(\text{SiMe}_2\text{O})_n\text{SiMe}_3$, $n = 0, 1, 2$ are marked by C.

species to give the k.i. (the reaction in Eq. (13c)). Thus the initiation proceeds with the mediation of a protic species, most often traces of water or silanol. Direct two-step reactions of **1** with water or silanol are also feasible.



There is a major difference between the condensation and redistribution systems which lies in the steady state concentration and the life-time of the k.i. Since in the MD_nM redistribution system the concentration of silanol species and water are at a very low level, the k.i. is not transformed to **3**. Thus, although it is formed slowly, the stationary summary concentration of its dormant and active forms is relatively high and does not change with the conversion. Therefore, the redistribution fits well for first-order kinetics. On the other hand the redistribution which accompanies the condensation proceeds according to second-order kinetics, as rates of both these competing reactions are related to the same stationary concentrations of the k.i. Thus, changing of initial concentrations is not likely to change the relative rates of condensation and redistribution in the silanol condensation system.

The mechanism proposed explains the complex effect of water addition on the MD₂M redistribution rate. Small amounts of water increase the rate because concentrations of protic acids are increased. However, too much water may decrease the concentration of k.i. because of its transformation to **3** and the possibility of irreversible hydrolytic decomposition. It is obvious that premixing of water with the catalyst suppresses the induction period as water produces **3** and acid needed for the formation of the k.i.

3. Experimental

3.1. Chemicals

Synthesis and characterization of basic monomer 1,1,3,3,3-pentamethyldisiloxane-1-ol (MDH), as well as

oligomers of Me₃Si[OSiMe₂]_nOSiMe₃ series, n = 1,2,3,4 used for the determination of response factor in gas chromatography were described earlier [38]. Purification of the solvents *n*-heptane and 1,1,2,2-tetrachloroethylene was described in Ref. [20].

3.2. Catalysts and kinetic studies

Both catalysts were received from the Dow Corning Europe Laboratory in Barry, UK. Purification of hexachloro-1λ-diphosphaza-1-enium hexachloroantimonate [Cl₃PNPCl₃]⁺SbCl₆⁻, **1** were made as described in Ref. [20]. *P*-Trichloro-*N*-dichlorophosphoryl phosphazene Cl₃PNP(O)Cl₂, **2**, was purified by vacuum resublimation at 10⁻³ mmHg which gave a crystalline fraction and a liquid residue. The crystalline fraction was pure **2** as indicated by its ³¹P NMR spectrum. The catalyst was distributed to vials under high vacuum which were fused out of the high vacuum line. The stock solution of **2** in sym-tetrachloroethane of concentration about 0.1 mol dm⁻³ was prepared. For this purpose the vial containing a known amount of **2** was placed together with a glass hammer into a large thick-walled ampoule fitted with a Rotaflo stopcock. The ampoule was connected to a high vacuum line. The required amount of sym-tetrachloroethane was distilled into the ampoule on the high vacuum line. The vial was crushed and the catalyst dissolved in (CHCl₂)₂. The stock solution was used for kinetic studies and for the NMR investigation. The stock solution of **1** was prepared in a similar way.

Kinetic studies, gas chromatographic analysis and the NMR analysis were performed in an analogous way to that described in Ref. [20].

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