Interactions of hexachlorodiphosphazenium ion with an alcohol and with some silicon–oxygen reagents and their role in the catalysis of polycondensation in silanol–alkoxysilane systems [1]

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Abstract

Condensation reactions of trimethylethoxysilane (MOEt) and pentamethyldisiloxanol in *n*-heptane catalysed by hexachloro-1λ-diphos-phaza-1-enium salts were studied. Although the substrate conversion vs. time dependences point to domination by heterofunctional condensation, the process is more complex. Homofunctional condensation as well as fast consecutive hydrolysis and ethanolysis strongly contribute to the overall process. Results of kinetic studies point to inhibition of these component reactions by an excess of MOEt. Interactions of the hexachloro-1λ-diphosphaza-1-enium salts with MOEt, ethanol and silanol were studied by ^{31}P NMR. It was demonstrated that a fast substitution reaction of chloride by ethoxy group takes place when ethanol or ethoxysilane is introduced into solutions of hexachlorodiphosphazenium salts. This process is responsible for the decrease in condensation activity of the catalyst.

Keywords: Oligophosphazenium ions; Catalysis of silanol condensation; Condensation of alkoxysilane with silanol; Reactions of hexachlorodiphosphazenium ion; Silicon; Phosphorus

1. Introduction

There has been a considerable interest in the chemistry of oligophosphazenium salts as they are intermediates in the synthesis of polyphosphazenes [1–7] and undergo interesting reactions, being strongly electrophilic reagents [8–11]. These salts have also been used as catalysts for the polycondensation and polymerization of siloxane polymers [12–14]. Thus, silanol-ended linear dimethylsiloxane oligomers may be transformed at ambient temperature within minutes into a polymer of high molecular weight above 10^5 using perchlorooligophosphazenium salts. Mechanisms of these important reactions have not yet been established. The key to understanding the catalysis in these pro-

cesses is to gain knowledge of the kinetics of the condensation as well as information on the reactivity of oligophosphazenium salts with silicon–oxygen compounds, such as silanol, siloxanes and alkoxysilanes. These reaction products may play an important role in the siloxane polycondensation or polymerization processes.

In this paper we present a kinetic study of the condensation of model silicon functional compounds catalysed by a model perchlorophosphazenium ion. We attempt to explain them using results of NMR studies of the interactions of these silicon compounds with the oligophosphazenium ions. The model system studied was the reaction of pentamethyldisiloxanol (MDOH) with trimethylethoxysilane (MOEt). Hexachlorodiphosphazenium salts [Cl$_3$PNPCl$_3$]$^+$ with complex anions PCl$_6^-$ or SbCl$_6^-$ were used as the catalysts since they have the simplest structure of the oligophosphazenium ions and both salts can be isolated in the pure state [14–19].

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[1] This paper is dedicated to Professor Robert Corriu in recognition of his great and important contribution to organosilicon chemistry.

2. Results and discussion

2.1. The kinetic features of the reaction of MDOH and MOEt catalysed with hexachlorophosphazenium salts

The condensation experiments were performed in n-heptane solution containing up to 5% of a catalyst solution in $Cl_2CHCHCl_2$. Conversion of both substrates as well as the formation of both heterofunctional condensation product and the homofunctional, MDOH + MDOH, condensation product were followed by gas chromatography. Some products of consecutive reactions, i.e. $Me_3SiOSiMe_2OEt$ (MDOEt) and in some cases Me_3SiOH (MOH) and $Me_3SiOSiMe_3$ (MM) were also traced. The first series of experiments was carried out at an initial MDOH:MOEt molar ratio close to one. Shapes of the substrate concentration vs. time plots are in accordance with domination of the reaction by heterofunctional processes (Fig. 1). Both substrates disappear at a similar rate to a high conversion and, to a reasonable approximation, according to the second-order kinetics. Moreover, the homocondensation product is present at very low concentrations (Fig. 2). However, the amount of the heterofunctional condensation product, octamethyltrisiloxane (MDM), is only about half of that expected from the conversion of the substrates. A
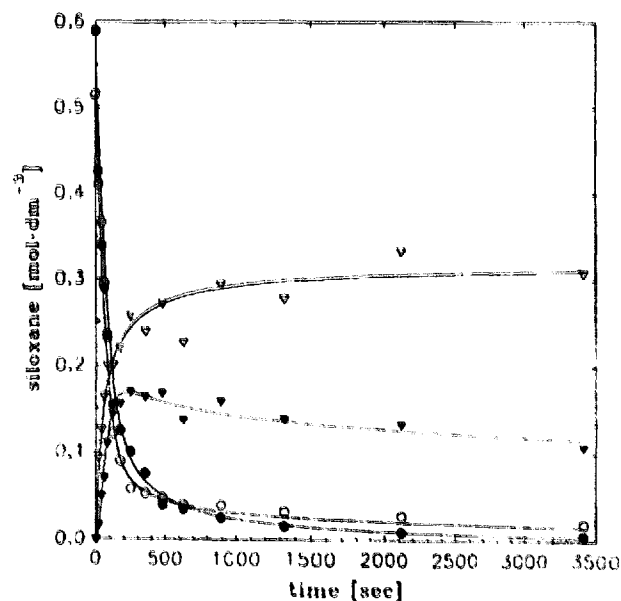

Fig. 2. Substrate-conversion–time dependences and product-formation–time dependences for the condensation of MDOH with MOEt catalysed by $[Cl_3PNPCl_3]^+$ PCl_6^-, 25 °C, $[Cl_3PNPCl_3]_0^+ = 3.04 \times 10^{-4}$ mol dm^{-3}. Experimentally determined concentrations are marked by: O, MDOH; ●, MOEt; ▽, MDM; ▼, MDOEt; □, MD₂M; ■, MOH; △, MM. Lines denote the corresponding dependences simulated according to general kinetic Eq. (11) including chemical Eqs. (1)–(9). Parameters are placed in Table 1 column 4.
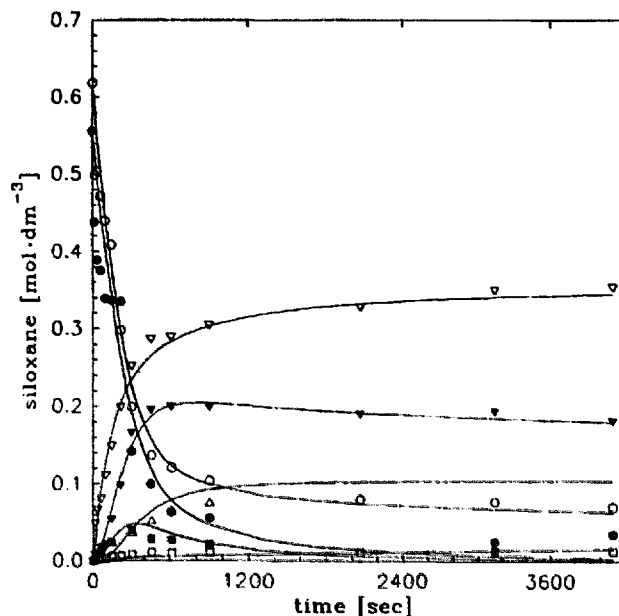

Fig. 1. Substrate-conversion–time dependences and product-formation–time dependences for the condensation of 1,1,3,3,3-pentamethyldisiloxane-1-ol (MDOH) with MOEt catalysed by $[Cl_3PNPCl_3]^+$ PCl_6^-, 25 °C, $[Cl_3PNPCl_3]_0^+ = 7.8 \times 10^{-4}$ mol dm^{-3}. Experimentally determined concentrations are marked by: O, MDOH; ●, MOEt; ▽, MDM; ▼, 1,1,3,3,3-pentamethyl-1-ethoxydisiloxane (MDOEt). Lines denote the corresponding dependences simulated according to general kinetic Eq. (11) including chemical Eqs. (1)–(9). Parameters are placed in Table 1 column 5.
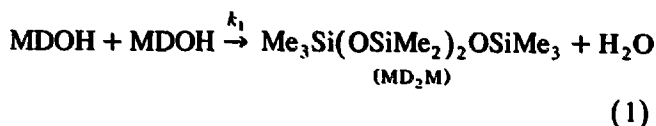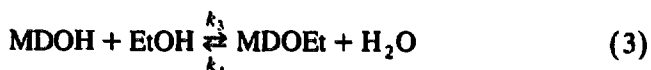
considerable quantity of ethoxypentamethyldisiloxane (MDOEt) is produced, indicating that extensive esterification of MDOH with ethanol or/and the direct exchange of functional groups between substrates takes place.

The fast esterification implies that fast hydrolysis of Me_3SiOEt also occurs since the hydrolysis of ethoxysilane is a well known reversible process. In order to check this hypothesis kinetic measurements were performed to determine the components which appear in the system at lower concentrations, such as trimethylsilanol (MOH), hexamethyldisiloxane (MM) and decamethyltetrasiloxane (MD_2M), product of homofunctional condensation. More intense and well separated peaks were analysed using a gas chromatograph with a filled column and a thermal conductivity detector, while less intense and overlapping peaks were analysed using a capillary column and a flame ionization detector. The production of seven silicon-based compounds was followed this way (Fig. 2). We found that MOH as well as its condensation product MM are formed indeed. The concentration of MOH reaches a maximum which is achieved in the early stages of the process. MOH is formed and quickly converted in the reaction, which means that it may be an important intermediate, although it appears at low concentration.
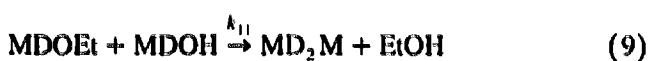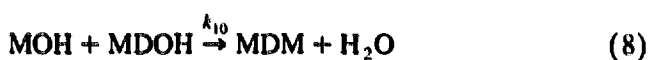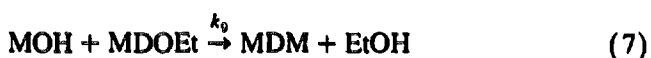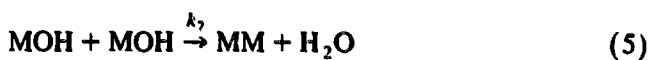
The system can be described by the 11 reactions shown in Eqs. (1)–(9), giving rise to a rather complicated kinetics analysis.

$$MDOH + MDOH \xrightarrow{k_1} Me_3Si(OSiMe_2)_2OSiMe_3 + H_2O$$

$$(MD_2M)$$

$$(1)$$

$$MDOH + MOEt \xrightarrow{k_2} Me_3SiOSiMe_2OSiMe_3 + EtOH$$

$$(MDM)$$

$$(2)$$

Functional group exchanges (involving starting materials, H_2O or EtOH) can also take place.

$$MDOH + EtOH \underset{k_4}{\overset{k_3}{\rightleftharpoons}} MDOEt + H_2O \qquad (3)$$

$$MOEt + H_2O \underset{k_5}{\overset{k_6}{\rightleftharpoons}} MOH + EtOH \qquad (4)$$

Secondary condensation reactions (involving one or two secondary reaction products) can be described as following:

$$MOH + MOH \xrightarrow{k_7} MM + H_2O \qquad (5)$$

$$MOH + MOEt \xrightarrow{k_8} MM + EtOH \qquad (6)$$

$$MOH + MDOEt \xrightarrow{k_9} MDM + EtOH \qquad (7)$$

$$MOH + MDOH \xrightarrow{k_{10}} MDM + H_2O \qquad (8)$$

$$MDOEt + MDOH \xrightarrow{k_{11}} MD_2M + EtOH \qquad (9)$$

Since equilibrium constants of the silanol condensation reactions are relatively high [20–22] the reactions in Eqs. (5)–(9) are assumed here to be irreversible.

According to the above scheme, the kinetic study of the overall process involves a differential equation system, the analytical resolution of which would be quite complicated. Thus, a computer simulation based on simplifying assumptions has been used. The basic assumption was that for all these reactions the order is equal to the molecularity. Thus, all the component reactions which can be described by Eq. (10):

$$substrate\, a + substrate\, b \xrightarrow{k} products \qquad (10)$$
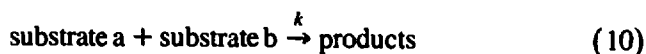
are represented by the following kinetic equation:

$$Rate = k[substrate\, a][substrate\, b] \qquad (11)$$

(For chemical Eqs. (1) and (5) the kinetic Eq. (11) is reduced to the form $Rate = k\,[substrate]^2$.)

The simulation was run to obtain the smallest deviations of experimental points from simulated curves. An example of the simulation is presented in Figs. 1 and 2. The fit is fairly good, taking into account that in some cases (Fig. 2) seven dependences were simulated using the same rate parameters. It was also shown that for a series of four runs performed with the same initial molar ratio (ca. 1:1), but with a variable initial catalyst concentration, fairly consistent rate constants are obtained (Table 1). Although the parameters were obtained on simplified assumptions and thus cannot be used as a quantitative measurement of the reactivity, they do give some idea about the contribution of various component reactions to the overall process. The apparently simple picture of the condensation process presented by the substrate-conversion–time dependences in

Table 1
Catalytic rate constants (third-order rate constants) of the component reactions of the condensation of MDOH with MOEt in n-heptane in 25 °C catalysed with hexachlorodiphosphazenium hexachlorophosphate at various catalyst concentrations, $[MDOH]_0/[MOEt]_0 = 1$, $[MDOH]_0 = 0.6\,mol\,dm^{-3}$. Parameters were obtained by the simulation according to the reaction scheme on Eqs. (1)–(9) assuming that orders of the reactions correspond to their molecularities

| Type of reaction	$[cat]_0 \times 10^{-4}$	Catalytic rate constants $(dm^6\,mol^{-2}\,s^{-1})$				
	Reaction	2.10	3.04 [a]	7.8	10	Average
≡SiOH + ≡SiOH	MOH + MOH	88	84	83	80	84
	MOH + MDOH	10	7.5	9.3	11	9.4
	MDOH + MDOH	0.4	0.15	1.4	0.4	0.6
≡SiOH + ≡SiOEt	MOH + MOEt	56	50	50	55	54
	MOH + MDOEt	20	18	18	20	18
	MDOH + MOEt	20	16.5	16.5	20	19
	MDOH + MDOEt	1.8	0.6	0.6	12	4
≡SiOH + EtOH	MOH + EtOH	93	87	87	94	91
	MDOH + EtOH	50	41	41	62	53
≡SiOEt + H₂O	MOEt + H₂O	257	160	160	291	247
	MDOEt + H₂O	99	60	60	111	110

[a] $[MDOH]_0/[MOEt]_0 = 0.85\,mol\,dm^{-3}$.
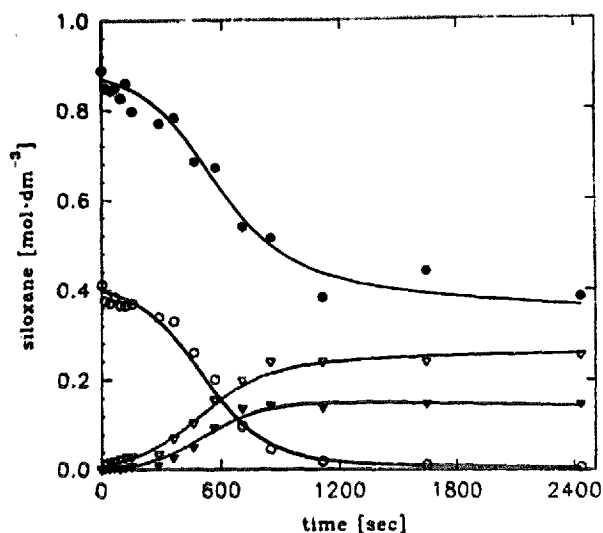
Fig. 3. Substrate-conversion-time dependences and product-formation-time dependences for the condensation of MDOH with MOEt catalysed by $[Cl_3PNPCl_3]^+ PCl_6^-$, 25°C, $[Cl_3PNPCl_3]_0^+ = 3.04 \times 10^{-4}$ mol dm^{-3}. Concentrations determined experimentally are marked by: ○, MDOH; ●, MOEt; ▽, MDM; ▼, MDOEt. Lines represent corresponding dependences simulated on assumption that $[Cl_3PNPCl_3]^+$ reversibly forms an unreactive product in reaction with MOEt and a reactive intermediate in reaction with MDOH and H_2O.

Fig. 1 results from a very complex reaction system including competing homofunctional and heterofunctional condensations. Reversible fast hydrolysis and al-

coholysis lead to functional group exchange. Corresponding reactions of functional monosilanes are much faster than those of functional disiloxanes, which explains the apparent domination of the heterofunctional condensation over the homofunctional one, while in reality the contribution from the homofunctional condensation is considerable.

When ethoxysilane MOEt was used in excess ($[MDOH]_0/[MOEt]_0 < 1$), S-shaped concentration–time curves were obtained, indicating that all component reactions were inhibited at early stage and accelerated as the process proceeded (Fig. 3). The simulation according to the simple scheme presented in Eqs. (1)–(11) did not give a satisfactory fit to the experimental data. Therefore, some modifications of the kinetic models were tested.

The best fitting of the simulation data to the experimental ones was obtained assuming the fast and reversible formation of the 1:1 complexes of the catalyst with ethoxysilane, silanol, water and ethanol. The complexes formed by the catalyst with silanol and water were thought to be the reactive intermediates, while those with ethoxysilane and ethanol were thought to be inactive. An example of the simulation for this kinetic model is shown in Fig. 3.

The results of these simulations give only approximate and qualitative characteristics of the process, as the reaction between catalyst and the species present in the medium takes place according to a much more
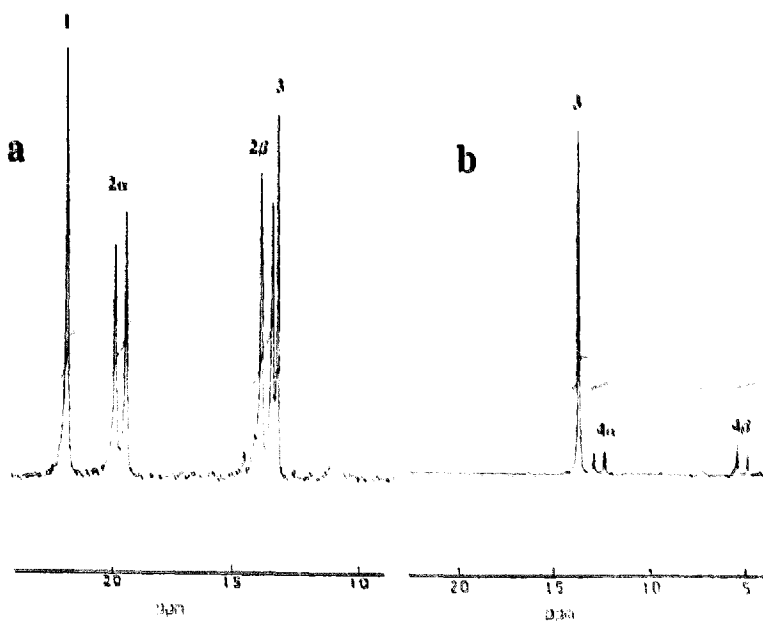

Fig. 4. ^{31}P NMR proton decoupled spectra of the solution of $[Cl_3PNPCl_3]^+ SbCl_6^-$, 0.02 mol dm^{-3}, in sym-tetrachloroethane to which ethanol was added. The solution was prepared and the spectra recorded at −20°C. (a) $[EtOH]_0/[Cl_3PNPCl_3]_0^+ = 1$; (b) $[EtOH]_0/[Cl_3PNPCl_3]_0^+ = 2.5$. Peaks are marked by numbers corresponding to those of compounds listed in Table 2.

complex mechanism, giving rise to irreversible various products showing different catalytic activity (see Section 2.2). Nevertheless, these simulation results suggest that the alkoxysilane inhibits the process and interacts with the catalyst producing the catalytically inactive species or a less active one. They also suggest that the catalyst forms intermediates with silanol and with water which do react towards the products.

Finally, it should be mentioned that MOEt is not only the inhibitor, responsible for the induction period of the reaction, but it effectively slows down the process. The homofunctional condensation of MDOH was found to proceed much more slowly in the presence of MOEt in

an equimolar mixture than in the absence of MOEt under the same conditions.

2.2. ^{31}P NMR studies of the interactions of Me_3SiOEt and $EtOH$ with hexachlorodiphosphazenium ions

There are few data in the literature about the interaction of oligophosphazenium ions with silicon oxygen reagents such as alkoxysilanes and silanols, and only a few reports about the interaction of these ions with alcohols [23]. The main phosphorus-containing products formed by the reaction of ethanol with hexachlorodiphosphazenium chloride and with hex-
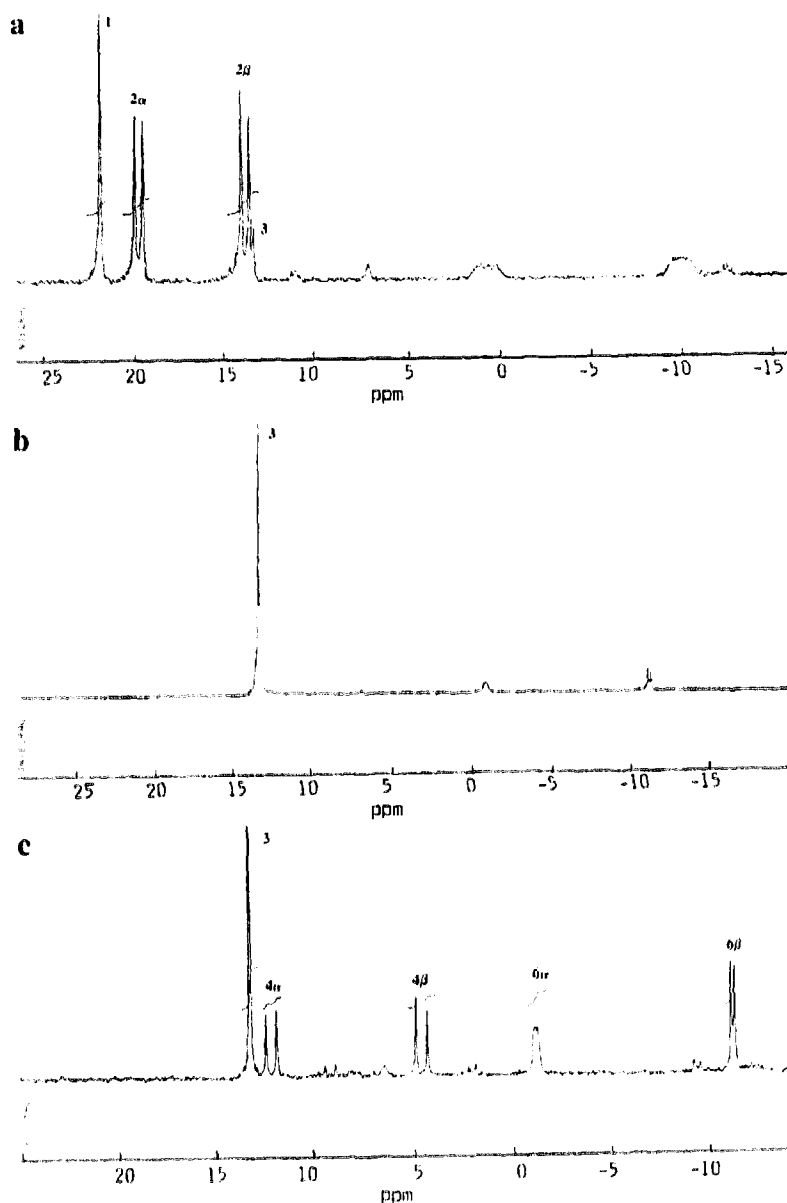

Fig. 5. ^{31}P NMR proton decoupled spectra of the solution of $[Cl_3PNPCl_3]^+$ $SbCl_6^-$, $0.02\,mol\,dm^{-3}$, in sym-tetrachloroethane, to which MOEt was introduced. The solution prepared and the spectra taken at $-20\,°C$. (a) $[MOEt]_0/[Cl_3PNPCl_3]_0^+ = 0.6$; (b) $[MOEt]_0/[Cl_3PNPCl_3]_0^+ = 3$; (c) $[MOEt]_0/[Cl_3PNPCl_3]_0^+ = 8$. Peaks are marked by numbers corresponding to those of compounds listed in Table 2.

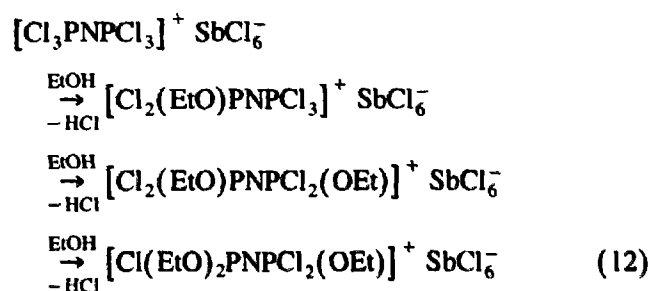achlorodiphosphazenium hexachlorophosphate were identified as P-trichloro-N-dichlorophosphorylphosphazene $(Cl_3P=N-P(O)Cl_2)$, $POCl_3$ and bis-dichlorophosphorylimide $Cl_2P(O)NHP(O)Cl_2$. No product originating from the substitution of Cl in the diphosphazene ion was detected. The first step of the reaction was suggested to be the addition of ^-OR to one of the phosphorus atoms of the cation leading to the formation of a neutral species containing a pentacoordinate phosphorus atom.

In order to identify the product of the first step of the reaction we studied, by ^{31}P NMR, the reaction of EtOH with $[Cl_3PNPCl_3]^+$ $SbCl_6^-$. This salt was preferred over the PCl_6^- salt because of solubility, its stability and the absence of a phosphors nucleus in the anion. The substrates were dissolved in sym-tetrachloroethane at $-20°C$ in different ratio at a concentration of $(0.01-0.03) \times 10^{-2}$ mol dm^{-3}. Spectra were recorded at $-20°C$ and are shown in Fig. 4(a) and (b).

Two doublets at 20 ppm and 14 ppm are attributed to the unsymmetrical $[(EtO)Cl_2PNPCl_3]^+$ cation. The assignment was confirmed by recording the spectra without proton decoupling; this showed that the signal at 14 ppm originated from the resonance of phosphorus bonded to the alkoxy group. The singlet at 13 ppm is assigned to the diphosphazenium cation symmetrically substituted with two ethoxy groups, while the two doublets at 12 ppm and 5 ppm present in the spectrum of reaction products at the higher ethanol to cation ratio are due to the presence of the tri substituted cation. These results clearly show that the reaction of ethanol with hexachlorodiphosphazenium cation involves as first step a nucleophilic substitution of the alkoxy group at

the phosphorus centre. Subsequent reactions lead to substitution of chlorine atoms by alkoxy groups with preference for the formation of the symmetrical product.

Thus a proposed mechanism can be described as the following:

$$[Cl_3PNPCl_3]^+ \ SbCl_6^-$$

$$\xrightarrow[-HCl]{EtOH} [Cl_2(EtO)PNPCl_3]^+ \ SbCl_6^-$$

$$\xrightarrow[-HCl]{EtOH} [Cl_2(EtO)PNPCl_2(OEt)]^+ \ SbCl_6^-$$

$$\xrightarrow[-HCl]{EtOH} [Cl(EtO)_2PNPCl_2(OEt)]^+ \ SbCl_6^- \qquad (12)$$
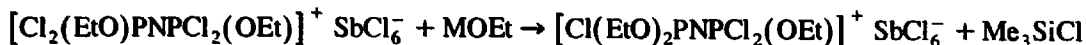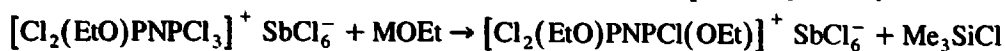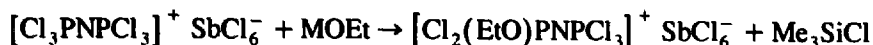
Higher substituted products may also be produced.

The interaction of the phosphazenium cation with Me_3SiOEt was studied in the same conditions. When 0.6 molar equivalent of MOEt was added to a solution of 2×10^{-2} mol dm^{-3} of $[Cl_3PNPCl_3]^+$ SbCl_6^-$ in sym-tetrachloroethane at $-20°C$ two doublets of the monoethoxy-substituted product immediately appeared. This product was coexisting with the remaining hexachlorodiphosphazenium cation (Fig. 5(a)). A small signal due to the symmetrical disubstituted cation is also observed. The addition of three molar equivalents of MOEt to the phosphazenium cation led to the almost sole formation of the disubstituted product (Fig. 5(b)). Small amounts of the trisubstituted product were formed in the reaction with five equivalents (Fig. 5(c)). The ^{31}P NMR data for these substitution products are gathered in Table 2. When an excess of MOEt (100 equivalents) was added to the hexachlorodiphosphazenium cation

Table 2
^{31}P NMR chemical shifts of products of reactions of $[Cl_3PNPCl_3]^+$ SbCl_6^-$ with Me_3SiOEt (MOEt) and EtOH; spectra taken in $(CHCl_2)_2$ at $-20°C$

No	Compounds	Chemical shift δ (ppm)	Coupling constant J_{PP} (Hz)
1	$[Cl_3PNPCl_3]^+$ SbCl_6^-	21.74	
2	$[Cl_3PNP(OEt)Cl_2]^+$ SbCl_6^- α β	α 19.62 doublet β 13.58 doublet	53.9
3	$[Cl_2(EtO)PNP(OEt)Cl_2]^+$ SbCl_6^-	13.14 singlet	
4	$[Cl_2(EtO)PNP(OEt)_2Cl]^+$ SbCl_6^- α β	α 12.08 doublet β 4.64 doublet	66.8
5	$[Cl_2(EtO)_2PNP(OEt)_2Cl]^+$ SbCl_6^- α β	4.74 singlet [b]	
6	$Cl_3PNP(O)Cl_2$	α −11.4 [a] β −0.9 [a]	20 [a]
7	$Cl_2(EtO)PNP(O)Cl_2$ α β	α −10.1 [a] β 1.5 [a]	38 [a]

[a] Sensitive to the presence of protic acids and to temperature in the presence of protic acid. [b] At 20°C.

and the temperature was raised to 20 °C the spectrum showed two doublets due to the trisubstituted product and a singlet at 4.7 ppm assigned to symmetrical dichlorotetraethoxydiphosphazenium ion (Fig. 6(b)).

Thus, it can be concluded that even in temperatures as low as −20 °C, relatively fast substitution reactions of chlorine atoms in oligochlorophosphazenium ions by alkoxy groups occur according to Eq. (13).

$$[Cl_3PNPCl_3]^+ \, SbCl_6^- + MOEt \rightarrow [Cl_2(EtO)PNPCl_3]^+ \, SbCl_6^- + Me_3SiCl$$

$$[Cl_2(EtO)PNPCl_3]^+ \, SbCl_6^- + MOEt \rightarrow [Cl_2(EtO)PNPCl(OEt)]^+ \, SbCl_6^- + Me_3SiCl$$

$$[Cl_2(EtO)PNPCl_2(OEt)]^+ \, SbCl_6^- + MOEt \rightarrow [Cl(EtO)_2PNPCl_2(OEt)]^+ \, SbCl_6^- + Me_3SiCl$$

$$[Cl(EtO)_2PNPCl_2(OEt)]^+ \, SbCl_6^- + MOEt \rightarrow [Cl(EtO)_2PNPCl_2(OEt)_2]^+ \, SbCl_6^- + Me_3SiCl$$

(13)

Introduction of the second ethoxyl group leads exclusively to the formation of the symmetrically substituted product. Substitution by a third group is more difficult than the second one. Thus, the presence of ethoxyl

group decreases the reactivity of the phosphorus moiety towards substitution on the phosphorus centre. Reactions of EtOH and Me₃SiOEt with the hexachlorodiphosphazenium ion may occur according to a
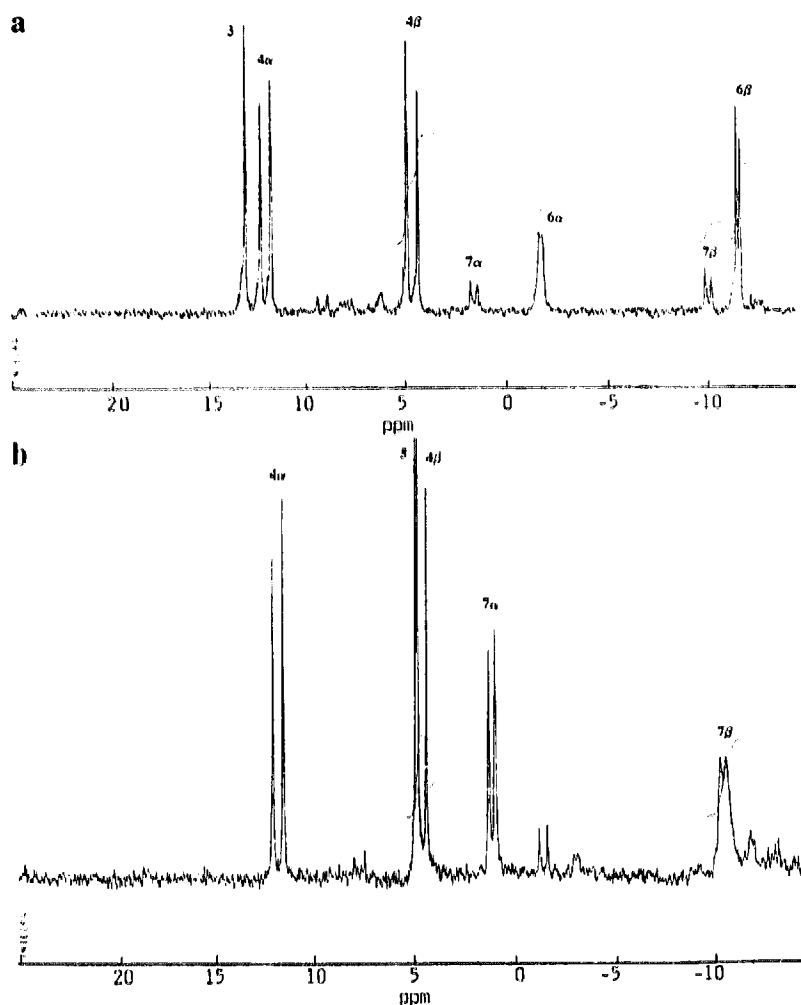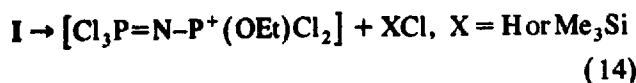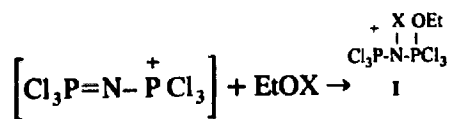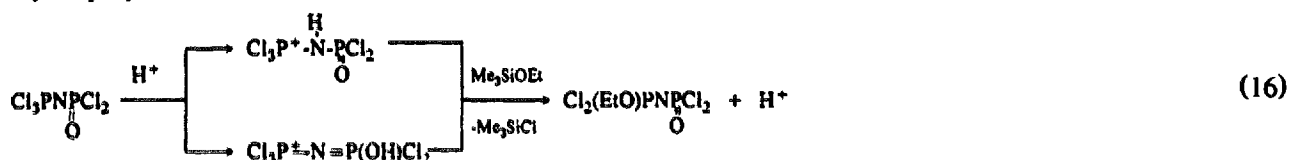

Fig. 6. ³¹P NMR proton decoupled spectra of the solution of [Cl₃PNPCl₃]⁺ SbCl₆⁻, 0.02 mol dm⁻³ in sym-tetrachloroethane to which 10² molar equivalent of MOEt was introduced: (a) spectra taken at −20 °C; (b) spectra taken after warming the solution to room temperature. Peaks are marked by numbers corresponding to those of compounds listed in Table 2.

similar mechanism involving nucleophilic attack on the phosphorus centre, resulting in the formation of a penta-coordinate phosphorus-atom-based addition product.
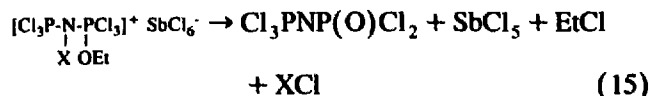
$$\left[Cl_3P{=}N{-}\overset{+}{P}Cl_3 \right] + EtOX \rightarrow \overset{\overset{\displaystyle + \; X \; OEt}{\displaystyle | \; |}}{\underset{I}{Cl_3P{-}N{-}PCl_3}}$$

$$I \rightarrow [Cl_3P{=}N{-}P^+(OEt)Cl_2] + XCl, \quad X = H \text{ or } Me_3Si \tag{14}$$

Addition of a large excess of MOEt to a $[Cl_3PNPCl_3]^+$ $SbCl_6^-$ solution at $-20°C$ leads to the formation of considerable amount of $Cl_3PNP(O)Cl_2$ giving rise to two doublets, $\delta = -1$, -11 ppm, $J_{PNP} = 20$ Hz (literature data are $\delta = -1$, -13 ppm, $J_{PNP} = 16{-}23$ Hz [24]). This compound appears together with the OEt-substituted phosphazenium products (Fig. 6(a)). It may be formed by the decomposition of the pentaco-ordinate phosphorus intermediate according to Eq. (15), similarly as proposed in Ref. [23].

$$\underset{X \; OEt}{\overset{[Cl_3P{-}N{-}PCl_3]^+ \; SbCl_6^-}{}} \rightarrow Cl_3PNP(O)Cl_2 + SbCl_5 + EtCl$$

$$+ XCl \tag{15}$$

On heating the sample to room temperature this phos-phorylphosphazene is almost fully transformed into its ethoxy monosubstituted derivatives (Eq. (16)) giving rise to two doublets in the ^{31}P NMR spectrum centred at 1.1 ppm and -10.4 ppm, $J_{PNP} = 38$ Hz, Fig. 6(b) (values found in the literature were $\delta = +1$ ppm, -11 ppm, $J_{PNP} = 36{-}42$ Hz [24]). Presumably the reaction takes an analogous course to the displacement of chlorine by the ethoxyl group in $[Cl_3PNPCl_3]^+$. Chemical shifts of both phosphorus in $Cl_3PNP(O)Cl_2$ were found to be sensitive to temperature. Some deshielding takes place as the temperature decreases. This observation implies that the phosphorylphosphazene undergoes fast re-versible protonation which may occur either on nitrogen or on oxygen. In the protonated form the $-PCl_3$ moiety shows a phosphonium cation character. Thus, the addi-tion-elimination may occur according to Eq. (16).

$$Cl_3PN\underset{O}{P}Cl_2 \;\; \overset{H^+}{\longrightarrow} \;\; \left[\begin{array}{c} Cl_3P^+{-}\overset{H}{N}{-}\underset{O}{P}Cl_2 \\[8pt] Cl_3P^{\pm}{-}N{=}P(OH)Cl_2^- \end{array} \right] \;\; \overset{Me_3SiOEt}{\underset{-Me_3SiCl}{\longrightarrow}} \;\; Cl_2(EtO)PN\underset{O}{P}Cl_2 + H^+ \tag{16}$$

Interestingly, the formation of the diethoxy-substituted N-phosphorylphosphazene product was not observed, in spite of a considerable excess of MOEt in the system. Thus, the substitution of the ethoxy group to phospho-rus in a neutral phosphorylphosphazene also decreased the reactivity of the substituted phosphorus moiety.
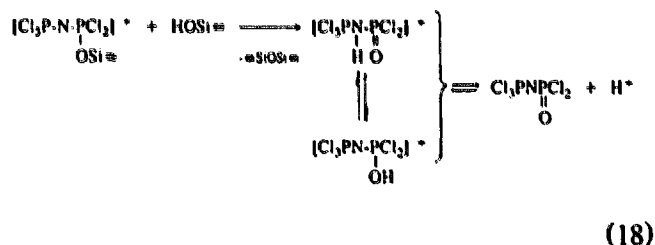
It is worth mentioning that $[Cl_3PNPCl_3]^+$ PCl_6^- un-dergoes similar reactions to those of Eqs. (13)–(15); however, the decomposition of the pentacoordinate in-termediate to neutral products (Eq. (15)) occurs more readily than with its antimonate analogue. A consider-able amount of the ethoxyl-substituted cation of the PCl_6^- salt was observed when the salt reacted with MOEt in $-40°C$.

We may expect silanols to behave like alkoxysilanes and alcohols in their interaction with the hex-achlorophosphazenium cation. Thus, $[Cl_3PNPCl_3]^+$ re-acts with a silanol according to the elimination addition reaction analogous to that presented in Eq. (14), which leads to the formation of the cation substituted by a siloxy group.
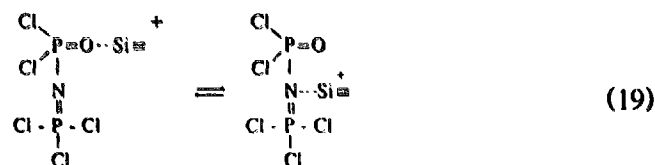
However, the formation of this cation has not been observed. P-trichloro-N-dichlorophosphoryl-phos-phazene was found to be the main product. It is formed according to Eq. (18).

$$\underset{OSi}{\overset{[Cl_3P{-}N{-}PCl_3]^+}{}} + HOSi \;\; \overset{}{\underset{-SiOSi}{\longrightarrow}} \;\; \left[\begin{array}{c} \underset{HO}{[Cl_3PN{-}PCl_3]^+} \\[8pt] \underset{OH}{[Cl_3PN{-}PCl_3]^+} \end{array} \right] \;\; \rightleftharpoons \;\; Cl_3PN\underset{O}{P}Cl_2 + H^+ \tag{18}$$

The reaction might be expected because such a siloxy-substituted phosphazenium cation is equivalent to a complex of sililenium ion (analogue of carbenium ion) with a neutral stable and relatively weak nucleophile (Eq. (19)) [25].

$$[Cl_3P{=}N{-}PCl_3]^+ + HOSi \rightarrow \underset{OSi}{\overset{[Cl_3P{=}N{-}PCl_3]^+}{}} \tag{17}$$

$$\begin{array}{c} \underset{Cl}{\overset{Cl}{>}}P{=}O{\cdots}Si{\equiv} \\ \underset{Cl{-}\underset{Cl}{\overset{\|}{P}}{-}Cl}{\overset{N}{|}} \end{array} \quad = \quad \begin{array}{c} \underset{Cl}{\overset{Cl}{>}}P{=}O \\ \underset{Cl{-}\underset{Cl}{\overset{\|}{P}}{-}Cl}{\overset{N{\cdots}Si{\equiv}}{|}} \end{array} \tag{19}$$

Thus, this species is extremely reactive towards any nucleophile being in the system, even a weak one, such as silanol, alkoxysilane, ethanol or water.

Reactions with these nucleophiles according to general scheme presented in Eq. (20) are likely to play an important role in the processes occurring in the system studied

$$\begin{array}{ccc}
\overset{|}{\underset{|}{-P}}\text{-O-H} & \overset{|}{\underset{|}{-P}}=O & \overset{|}{\underset{|}{-P}}\text{-O-Si}\equiv \\
N & \rightleftharpoons \quad NH \quad \overset{\equiv SiOX}{\longrightarrow} & N \\
\parallel & \parallel \ + & \parallel \\
-P- & -P- \quad \text{-HOX} & -P- \qquad X = H \text{ or Et}
\end{array}$$

(21)

reaction observed:
X = Si≡, Y = H   condensation
X = Si≡, Y = Et   condensation
X = H, Y = H   hydrolysis
X = Et, Y = H   ethanolysis

(20)
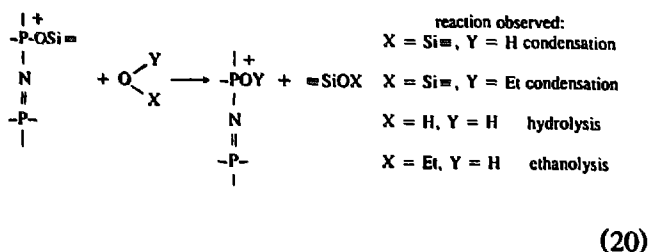
During the catalysis the $-^{+}\overset{|}{\underset{|}{P}}OY$ centre must be transformed back into the silyl centre. The $-^{+}\overset{|}{\underset{|}{P}}OH$ centre formed either in the reaction of Eq. (20) or directly by the hydrolytic substitution of $-\overset{|}{\underset{|}{P}}-Cl$ group or by $-\overset{|}{\underset{|}{P}}=O$ protonation, may be converted relatively easily by the reaction in Eq. (21).
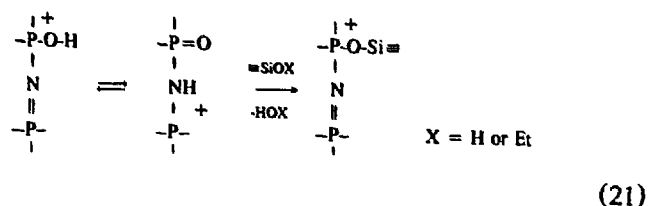
The analogous transformation of $-\overset{|}{\underset{|}{P}}-OEt$ centre, which occurs as a result of the reaction in Eq. (20) or directly by substitution of Cl in the oligophosphazenium ion, seems to be more difficult and proceeds much more slowly. Thus, the $-\overset{|}{\underset{|}{P}}=N-\overset{|}{\underset{|}{P}}{}^{+}-OSi\equiv$ and $-\overset{|}{\underset{|}{P}}=N-\overset{|}{\underset{|}{P}}{}^{+}-OH \rightleftharpoons -\overset{|}{\underset{|}{P}}{}^{+}-NH-\overset{|}{\underset{|}{P}}=O$ are the true intermediates obviously able to react towards products, while the formation of $-\overset{|}{\underset{|}{P}}=N-\overset{|}{\underset{|}{P}}{}^{+}-OEt$ impedes the catalytic reactions.

In order to verify these mechanistic concepts and to propose a unified scheme of the process, a low-temperature ^{31}P NMR experiment was performed in conditions close to those used in the kinetic measurements. A high excess of 3:1 mol/mol mixture of MOEt with MDOH was added to a solution of hexachlorophosphazenium antimonate at $-20\,^{\circ}$C. The spectrum (Fig. 7) showed signals of only two phosphorus-containing products. Two doublets $\delta = -9.5$ ppm and 2 ppm, $J_{PNP} = 38$ Hz,
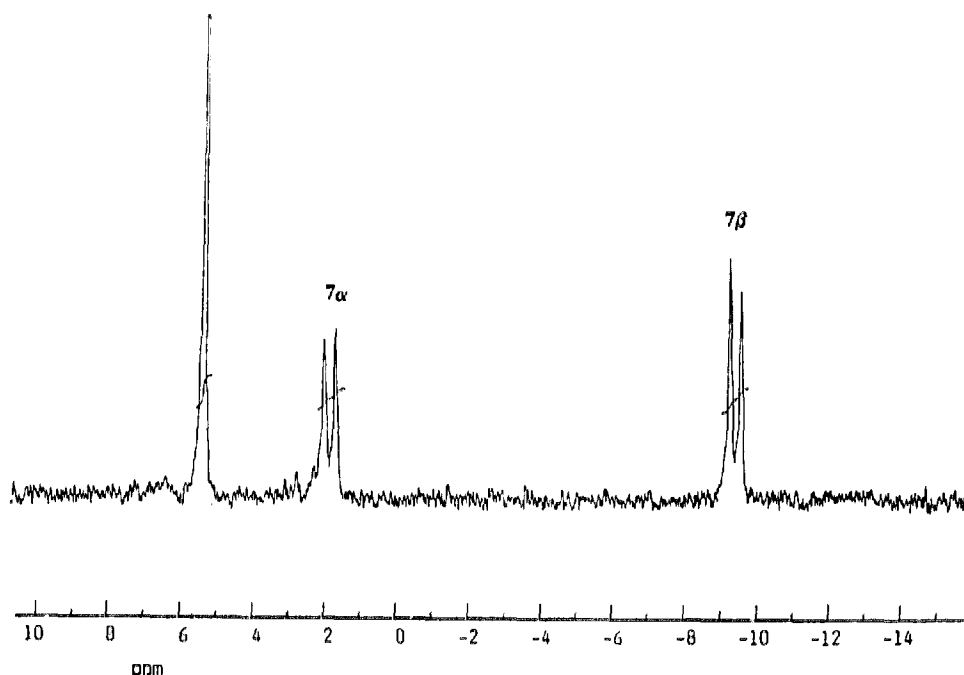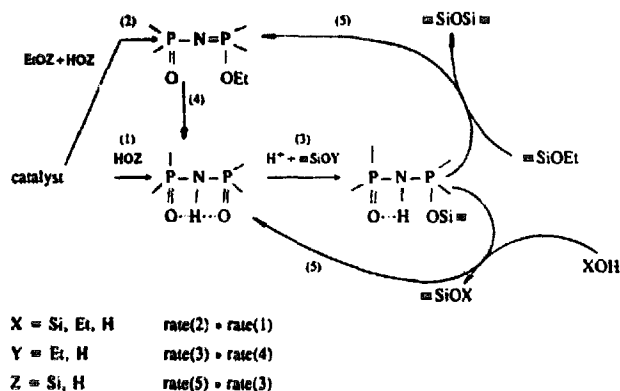

Fig. 7. ^{31}P NMR proton decoupled spectra of the solution of $[Cl_3PNPCl_3]^{+} SbCl_6$, 0.02 mol dm^{-3} in *sym*-tetrachloroethane to which 25 molar equivalents of MDOH and 75 molar equivalents of MOEt were introduced. The solution prepared and spectra taken at $-20\,^{\circ}$C. Peaks are marked by numbers corresponding to those of compounds listed in Table 2.

Scheme 1.

were assigned to $Cl_2(EtO)PNP(O)Cl_2$ while a singlet at $\delta = 5.5$ ppm was most probably due to $P(O)Cl_3$, as the addition of this compound to the system strengthened the signal without any change in the rest of the spectrum. Thus, indeed the only species which could be regarded as a form of the catalyst bears an ethoxyl substituent. In addition, the experiment showed clearly that the structure $>P(O)NP\equiv$, considered as the active form of the catalyst in Eq. (21), is rapidly formed even at $-20\,^\circ C$. Therefore, the schemes of Eqs. (20) and (21) themselves do not explain the induction period observed when excessive amounts of MOEt are used. The mechanism presented in Eqs. (20) and (21) is oversimplified as it does not fully take into account the role of the other phosphorus centre in the catalyst. The reactions in Eqs. (20) and (21) are likely to involve another oxyphosphoryl group to assist in proton transfer; receiving proton from reactants (a) and transferring it to products (b) as shown below.
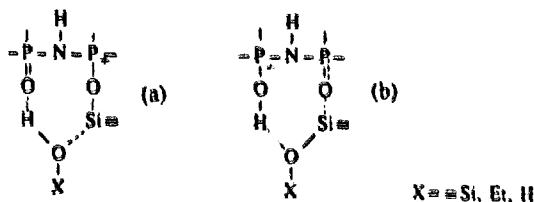
This oxyphosphoryl group must be generated on the phosphorus atom neighbouring to the reaction centre. The presence of the ethoxyl substituent at this phosphorus makes it difficult to form this $\equiv P(O)$ group, which may be at the origin of the observed induction period of condensation.

The reversibility of the reactions in Eq. (13) was checked by adding a large excess (10:1 mol/mol) of Me_3SiCl to the previously prepared solution of the mixture of the monoethoxy- and diethoxy-substituted phosphazenium ion. Hexachlorophosphazenium ion was not reformed, and proportions of intensities of the phos-

phorus resonance signals remained almost unchanged. Therefore, the equilibrium is quite shifted towards the substitution products. This result calls in question the assumption that stationary concentration of the ethoxy-substituted intermediates are controlled by this equilibrium. The process is more complex than it was assumed to be in the modified procedure of kinetic simulation. A general simplified scheme of the process can be drawn from all experimental observations and is presented in Scheme 1. Step (1) consists in either hydrolysis, or the reactions of Eqs. (17) and (18). Step (2) involves the reaction in Eq. (13) competing with the reactions of Eqs. (17) and (18). Step (3) is the reaction in Eq. (21), while step (5) is the reaction in Eq. (20).

3. Experimental section

3.1. Chemicals

Me_3SiOEt provided by Dow Corning was purified by distillation over column. Its purity was higher than 99% as checked by gas chromatography.

$Me_3SiOSiMe_2OH$ was synthesized by hydrolysis of 1,1,1,3,3-pentamethyldisiloxane (ABCR reagent grade) catalysed by Aldrich 5% palladium on activated carbon and purified by distillation. The purity checked by gas chromatography was 99%.

Compounds used for determination of response factors in gas chromatography, i.e. $Me_3Si[OSiMe_2]_n$-$OSiMe_3$, $n = 0, 1, 2$, $Me_3SiOSiMe_2OEt$ and Me_3SiOH were obtained and purified using well known procedures. Their purities determined by gas chromatography were at least 99.5%.

Solvents were purified according to usual procedures. Thus, n-heptane was repeatedly shaken with concentrated H_2SO_4, washed with water, then with a solution of Na_2CO_3 and again several times with water. It was then dried over $CaCl_2$ and distilled from $CaCl_2$ to an ampoule with a Rotaflo stopcock. 1,1,2,2-Tetrachloroethane was repeatedly shaken with concentrated H_2SO_4, thoroughly washed with water, kept over K_2CO_3, then dried over CaH_2 and distilled from CaH_2 to an ampoule with a Rotaflo stopcock under argon.

Hexachlorodiphosphazenium salts were synthesized in the Dow Corning Laboratory, Barry. All operations with these salts were carried out either in a dry box under pure nitrogen or using a high vacuum line. Thus, crystalline $[Cl_3PNPCl_3]^+$ $SbCl_6^-$ was rinsed with pure methylene chloride, dried and then distributed on a high vacuum line to thin-walled vials, which were fused out from the high vacuum line. The vial containing a known amount of the salt was placed together with a glass hammer into a large thick-walled ampoule fitted with a Rotaflo stopcock and a glass joint through which it was connected to the high vacuum line. A known amount of

the solvent ($Cl_2CHCHCl_2$) was distilled on this vacuum line into the ampoule. The vial was crushed and the solution of $(0.2-0.4) \times 10^{-2}$ mol dm^{-3} of the salt was made. It served as the stock solution for the preparation of solutions for kinetic studies or was used for the NMR investigations. The ^{31}P NMR spectrum of this solution showed only one signal at 22.4 ppm. The solution of $[Cl_3PNPCl_3^+]PCl_6^-$ was prepared in an analogous way.

3.2. Kinetic studies

The condensation process was carried out in a glass 10 ml reactor fitted with a three-way precision stopcock. The reactor was purged with pure argon and charged with the required amounts of solvent, standard for gas chromatography (tridecane) and substrates by means of precision Hamilton syringes keeping a stream of argon through the stopcock. The reactor was thermostated by Julabo 25 thermostat, keeping the temperature constant within ±0.1 °C. The zero sample was withdrawn by means of Hamilton syringe and then the required volume of the stock solution of catalyst was introduced by precision Hamilton syringe. Samples (50 μl) were withdrawn with a Hamilton syringe at required time intervals. They were introduced to Ependorfer tubes containing quenching agent (i.e. 20 μl of Et_3N). Then, samples were subjected to gas-chromatographic analysis.

3.3. Gas chromatography

Gas chromatography analyses were performed with a Jeol JC6 1100 gas chromatograph working with Takeda Riken 2215 A integrator. The chromatograph was fitted with a thermal conducting detector, a column ($l = 2$ m, $d = 3$ mm) filled with 10% OV 101 on Gas Chromosorb Varaport 60/80 mesh, temperature 30–250 °C, programmed 15° min^{-1}, detector temperature 260 °C, injector temperature 220 °C. Tridecane was used as internal standard. Concentrations of Me_3SiOH and $Me_3SiOSiMe_3$ which appeared at lower concentrations were determined using a Hewlett Packard 5890 chromatograph working with an HP 3396 S integrator. It was fitted with a flame ionization detector, capillary column ($l = 30$ m, $d = 0.53$ mm) filled with HPI, temperature 50–280 °C programmed 15° min^{-1}.

3.4. NMR spectroscopy

^{31}P NMR analysis were made with Brucker 300 MSL instrument working at frequency 121.49 MHz.

3.5. Computer simulation

Computer simulations were performed with a PC/386 computer using a program written in TURBO PASCAL 6.0. The system of kinetic equations was numer-ically solved using the Runge–Kutta–Fehlberg method [26]. The optimization of rate constants was carried out using the Rosenbrock procedure [27], minimizing the sum of the squares of relative deviations of simulated concentrations of MDOH, MOEt, MDOEt, MDM, MM, and MD_2M from experimental values.

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