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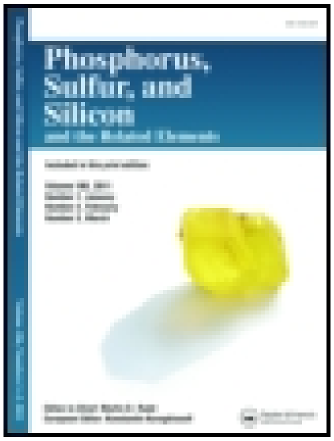

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CYCLIC PHOSPHONITRILIC COMPOUNDS BEARING —N=PCl$_3$ GROUP AS HOMOGENOUS CATALYST TOWARDS THE SILANOL CONDENSATION

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CYCLIC PHOSPHONITRILIC COMPOUNDS BEARING –N=PCL₃ GROUP AS HOMOGENOUS CATALYST TOWARDS THE SILANOL CONDENSATION

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Condensation reactions of 1,1,3,3,3 pentamethyldisiloxane-ol (MDH), in toluene catalysed by two types of phosphonitrilic catalyst bearing a phosphazene –N=PCl$_3$, were studied using sampling and gas chromatographic analysis method. The condensation kinetics reactions were compared for both phosphazene compounds. The process is selective, leading to linear decamethyltetrasiloxane MD$_2$M, (where D denotes the dimethylsiloxane unit and M denotes the trimethyloxysilane unit) as almost the exclusive primary product. The mechanisms of the MDH condensation are discussed using the ^{31}P NMR sampling technique.

Keywords: Cyclic phosphazenes; polysiloxane; reactivity mechanism; silanol condensation

INTRODUCTION

There has been considerable interest in the chemistry of phosphazene compounds as catalysts for the polycondensation and polymerization of siloxane polymers.[1–16] 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. The advantage of using these catalysts is that the product of the polycondensation does not contain cyclic

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oligosiloxanes. These phosphonitrile chloride oligomers also promote the redistribution of linear polysiloxanes without formation of a significant amount of cyclic species.[17,18] The key to understanding the catalysis in this process is to gain knowledge of the kinetics of the condensation as well as information on the reactivity of phosphazene compounds with silicon–oxygen compounds such as silanol, siloxanes, and alkoxysilanes. According to the recent literature, the mechanisms of these important reactions have extensively been investigated by Chojnowski et al.[19,20] We should also note the theoretical study concerning the condensation reactions in silanol-water clusterrs using B3LYP and MP2 methods, which have been recently investigated by Ignatev et al.[21] The aim of this study was to explore the catalytic effect of water in the $2H_3SiOH + nH_2O$ ($n = 1, 2$) systems.

As part of our study, we have recently studied the kinetics and mechanism of reaction between oligosiloxanes and P-Trichloro-N-dichlorophosphoryl monophosphazene $Cl_3P{=}N{-}P(O)Cl_2$.[22] The purpose of this work was to explore the action of the $-N{=}PCl_3$ unit toward the oligosiloxane compounds and the role of the reaction products in the siloxane polycondensation or redistribution process. Indeed, it was demonstrated in this work that only the monosubstitution of a chlorine atom by the $-(OSiMe_2)_n$-$OSiMe_3$ species $n = 0, 2, 3$ with elimination of trimethylchlorosilane occurred, leading to the derivatives $Cl_2OP{-}N{=}PCl_2O$-$(SiMe_2$-$O)_n\ SiMe_3$. A two-step mechanism is proposed, consisting in a nucleophilic substitution, involving a tricoordinate phosphazenium intermediate, followed by the formation of an active ionic centre probably an oxonium ion.

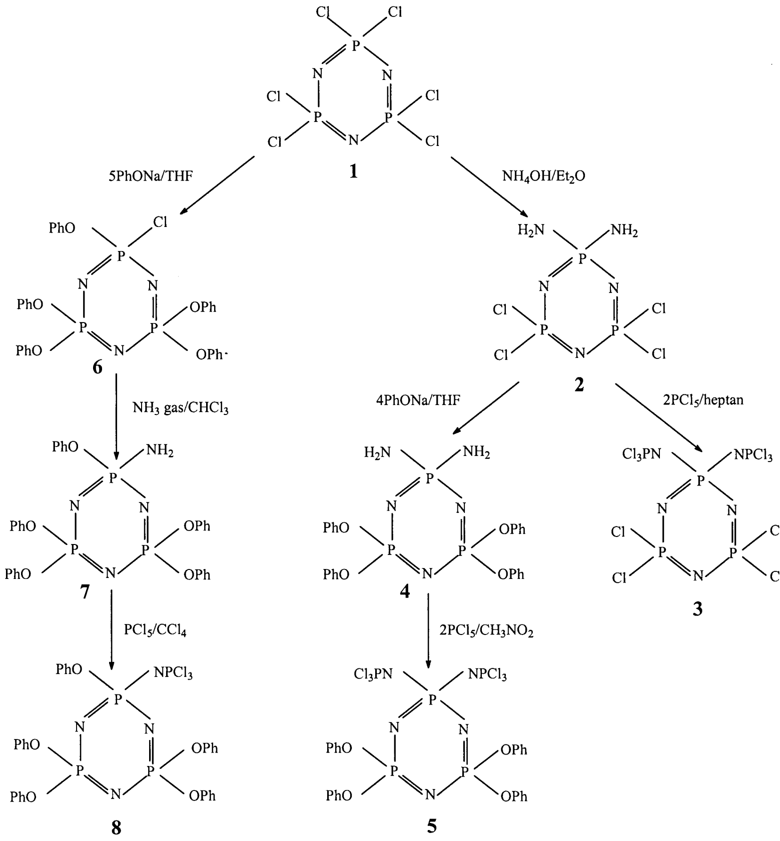
In this article we present a kinetic study of the model silicon functional compound pentamethyldisiloxane-ol (MDH) catalyzed by model cyclic phosphazene compounds bearing a ($-N{=}PCl_3$) group.

The preparation of different cyclic phosphazenes compounds (**2**)–(**8**) are described in (Scheme 1):

1,1,3,3,3-Pentamethyldisiloxane-1-ol (MDH) was used as the model substrate in this polycondensation study because it is the simplest stable oligosiloxanol and its condensation leads to only one product, MD_2M, where D and M denote the dimethylsiloxane and M the trimethylsiloxane units, respectively, according to Equation (1):

$$\underset{\text{(MDH)}}{2\ Me_3SiOSiMe_2OH} \longrightarrow \underset{MD_2M}{Me_3Si(OSiMe_2)_2OSiMe_3} + \text{H2O} \qquad (1)$$

Well-defined cyclic phosphazene species containing two or one $-N{=}PCl_3$ units (**3**) and (**8**), respectively, were selected to promote the MDH condensation. The cyclic phosphazene compounds (**3**) and (**8**) are



SCHEME 1 Synthesis of cyclic phosphazene compounds (**2**)–(**8**).

well-known and well-characterized chemical compounds, their purity was controlled by ^{31}P NMR (nuclear magnetic resonance).

RESULTS AND DISCUSSION

Kinetics of Condensation of 1,1,3,3,3-Pentamethyl-disiloxane-1-ol

Reactions were performed in toluene. The initial concentration of $[\mathrm{MDH}]_0$ was 1 Mol/l and 0.7 mol/l in the cases of the catalysts (**3**) and (**8**), respectively. In both cases the concentration of the catalyst was 10^{-3} mol/l. Kinetics were investigated by sampling the reaction mixture and determining the substrate MDH concentrations by gas chromatography. Reactions were followed to a conversion of 60–98%.

Since equilibrium constants of the silanol condensation reactions are relatively high,[23–25] the reaction in Equation (1) is assumed here to be irreversible. In this case, Equation (1) is represented by the following kinetic equation:

$$\text{Rate} = -\frac{1}{2}\frac{d[\text{MDH}]}{dt} = \text{K}.[\text{MDH}]^{\alpha}.[\text{cata}]^{\beta}$$

$$m = \alpha + \beta$$

where m presents the global order of the reaction, α and β represent the partial orders, and K is the rate constant of the condensation reaction.

If we consider that the concentration in catalyst remains constant, the rate is reduced to the form

$$\frac{-d[\text{MDH}]}{dt} = 2\text{K}_{\text{app}}[\text{MDH}]^{\alpha}, \quad \text{with } \text{K}_{\text{app}} = \text{K}.[\text{cat}]^{\beta}$$

K_{app} being the apparent rate constant.

Study of the Catalytic Activity of (3)

The influences of the initial concentration of compound (**3**), of the temperature and of the HCl (stemming from the hydrolysis of the exocyclic P—Cl bonds) on the kinetics of the reaction were examined.

Determination of the Partial Orders with Regard to the MDH and to the Catalyst

At first, we studied the kinetics of the reaction at 40°C with initial concentrations in MDH and (**3**) around 1 and 10^{-3} mol/l, respectively.

The reaction proceeds according to the second-order kinetic law for the catalyst (**3**) until 80% MDH conversion (Figures 1 and 2). Afterwards the condensation reaction slowed down, presumably as a result of the irreversible loss on decomposition of an active form of the catalyst. The constant rate deducted from the curve of Figure 2 is $\text{K}_{\text{app}} = 1.45\ 10^{-3}$ l. $\text{mol}^{-1}.\text{s}^{-1}$.

A considerable amount of water was released during the reaction, and a dispersed water phase appeared in the early stage of the process. Thus, a stationary water concentration in the organic phase is established very soon after the beginning of the reaction. For this purpose, this kinetic reaction was compared with that of a MDH condensation carried out at 40°C in the toluene, catalyzed by HCl in the concentration of 10^{-2} mol/l. Indeed, the hydrolysis of (**3**) led to the formation of such acid, which catalyzes the condensation of silandiols.[26] The HCl

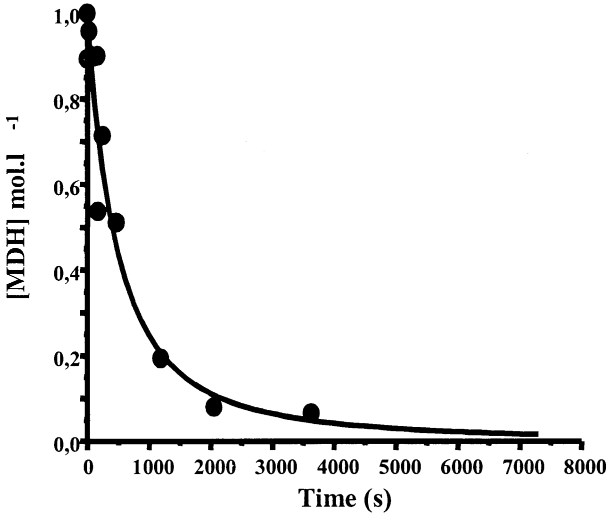


FIGURE 1 Substrate conversion time dependences for the condensation of MDH catalyzed by (**3**) in toluene at 40°C, $[\text{MDH}]_0 = 1$ mol. l^{-1}, $[(\mathbf{3})] = 10^{-3}$ mol.l^{-1}.

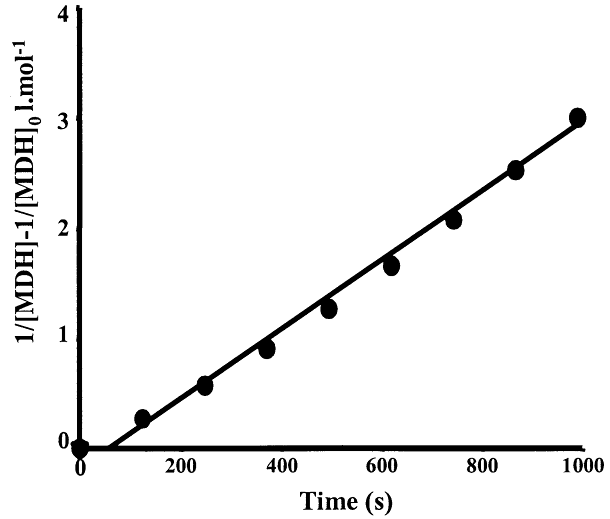


FIGURE 2 The second-order plot for the substrate conversion versus time.

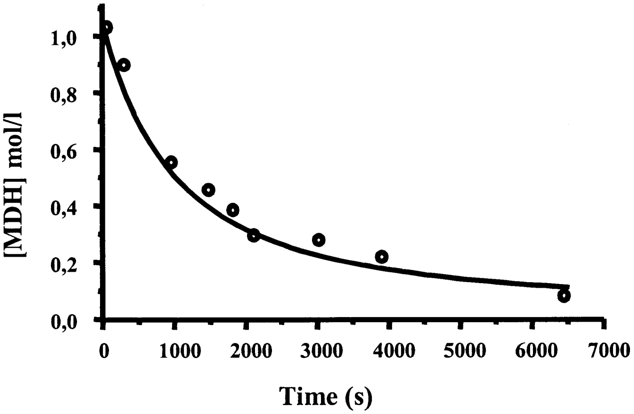


FIGURE 3 Substrate conversion time dependences for the condensation of MDH catalyzed by HCl in toluene at 40°C, $[\mathrm{MDH}]_0 = 1\ \mathrm{mol.l^{-1}}$, $[\mathrm{HCl}] = 10^{-2}\ \mathrm{mol.l^{-1}}$.

concentration chosen in this study corresponds to the total concentration of chlorine atoms in compounds (**3**).

The curves [MDH] = f(time) and $\frac{1}{[\mathrm{MDH}]} - \frac{1}{[\mathrm{MDH}]_0}$ = f(time) are represented in Figures 3 and 4. In this case, we should note that the reaction also obeys a second-order kinetic law, with an apparent rate constant $K_{app} = 0.9\,10^{-3}\ \mathrm{mol^{-1}.s^{-1}}$.

The necessary time to have the conversion of 80% of the MDH is about 3600 s. This comparison shows that MDH's condensation in the presence of (**3**) cannot be explained by a simple catalysis of HCl produced from the hydrolysis of the P—Cl bonds.

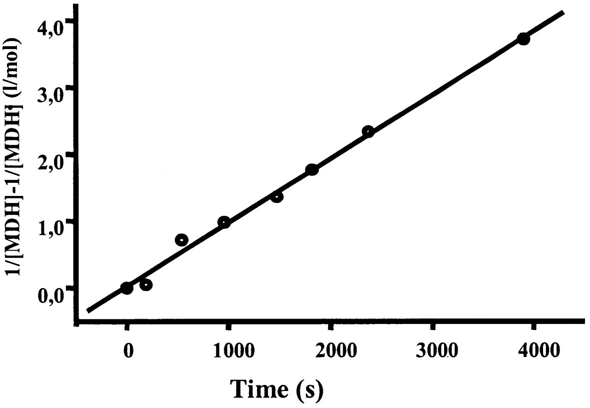


FIGURE 4 The second-order plot for the substrate conversion versus time.

TABLE I Comparison of Second-Order Rate Constant for the Condensation of MDH in the Presence of (**3**), $[MDH]_0 = 1$ mol l^{-1}

[3] mol.l^{-1}	Kapp (l.mol^{-1}.s^{-1})
5.10^{-3}	$1.375.10^{-3}$
10^{-3}	$0.3.10^{-3}$
$0.85.10^{-3}$	$0.25.10^{-3}$
$0.5.10^{-3}$	$0.143.10^{-3}$

A series of runs was also performed at different catalyst concentrations (5.10^{-3}, 10^{-3}, $0.85.10^{-3}$, and 0.5. 10^{-3} mol/l) at 25°C. The initial concentration in MDH in all cases was equal to 1 mol/l. The apparent rate constant for each experiment is summarized in Table I. The curve in Figure 5 represents the evolution of Ln K_{app} versus Ln (**3**). The slope in a double logarithmic plot of the rate-concentration dependance gives a value equal to 1, which would tend to show that a mole of (**3**) catalyses the reaction of condensation of two MDH moles. It is interesting to note that this value is different from that proposed by Chojnowsky et al.,[20] who quoted a value of 1.5 for both catalysts $Cl_3P{=}N{-}P(O)Cl_2$ (P_2O) and $[Cl_3P{=}N{-}PCl_3]^+[SbCl_6]^-$ (P_2^+).

The results of the experiments performed at different temperatures allowed the estimation of the activation energie of the catalyst. Indeed,

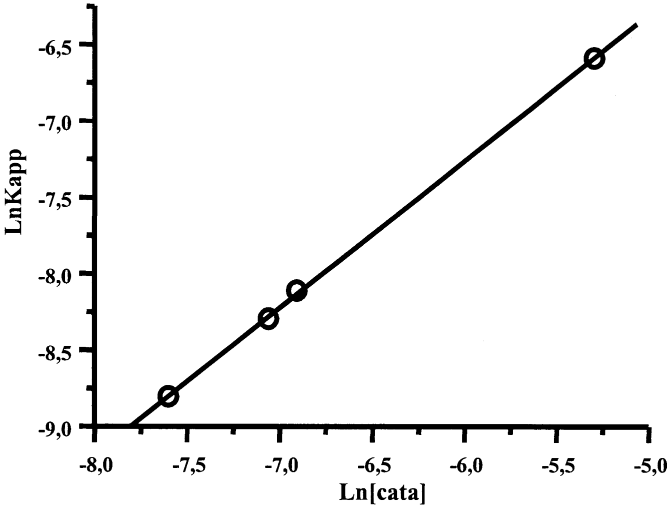


FIGURE 5 Dependence of Ln of the second-order rate constant on the Ln of the concentration of catalyst for the condensation of MDH in the presence of (**3**), $[MDH]_0 = 1$ mol l^{-1}, 25°C.

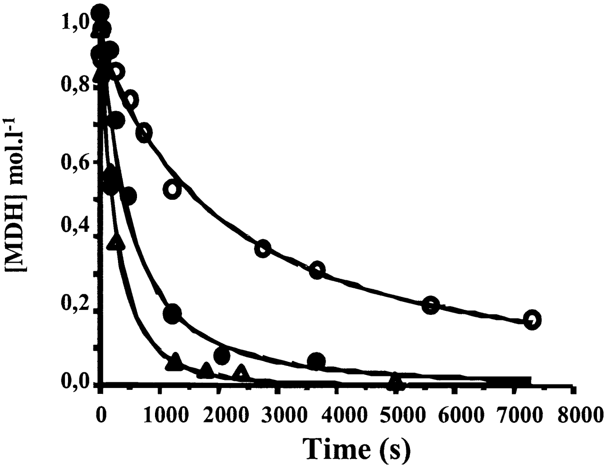


FIGURE 6 Substrate conversion time dependences for the condensation of MDH catalyzed by (**3**) at different temperatures in toluene, $[MDH]_0 = 1$ mol l^{-1}, $[(3)] = 10^{-3}$ mol l-1, ○ 298 K, ● 313 K, ▲ 333 K.

three studies of the reaction of condensation were made at three different temperatures: 25, 40, and 60°C, with initial concentrations of MDH and catalyst of $[MDH]_0 = 1$ mol/l and $(\mathbf{3}) = 10^{-3}$ mol/l. In Figures 6 and 7 are represented the curves [MDH] = f(time) and $\frac{1}{[MDH]} - \frac{1}{[MDH]_0} =$ f(time). We can note that the rate of condensation increases with the

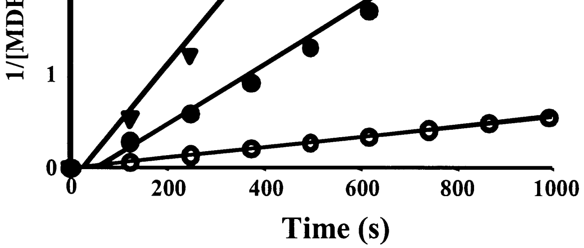


FIGURE 7 Second-order plot for the condensation of MDH in toluene in the presence of (**3**) at different temperature, $[MDH]_0 = 1$ mol l^{-1}, $[(\mathbf{3})] = 10^{-3}$ mol l^{-1}, ○ 298 K, ● 313 K, ▲ 333 K.

TABLE II Comparison of Second-Order Rate Constant for the Condensation of MDH Catalyzed by (**3**) at Different Temperatures, $[\mathrm{MDH}]_0 = 1\ \mathrm{mol\ l^{-1}}$, $[(\mathbf{3})] = 10^{-3}\ \mathrm{mol\ l^{-1}}$

Temperature (K)	K_{app} ($\mathrm{l.mol^{-1}.s^{-1}}$)
298	$0.3.10^{-3}$
313	$1.45.10^{-3}$
333	$2.95.10^{-3}$

temperature. The values of the apparent constant rate according to the temperature are summarized in Table II.

Even if it is not possible to determine the real value of the energy of activation, Arrhénius's law nevertheless allows us to calculate its apparent value connected with K_{app} according to the following relation:

$$K_{app} = K_0 \exp^{-E_{app}/RT}$$

in which E_{app} represents the energy of activation and K_0 the factor of frequency. The curve of Figure 8 represents the variation of the Ln K_{app} versus $\frac{1}{T}$. We found a value of 12.70 kcal/mol, which is very close to that determined by Chojnowsky et al.[20] for a similar study carried out with catalysts P_2NOCl_5 and $[PCl_3NPCl_3]^+[SbCl_6]^-$ (9.1 and 12.9 kcal/mol, respectively).

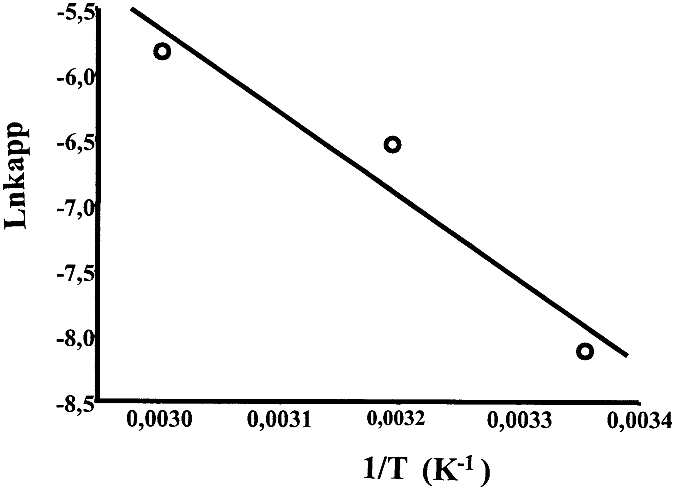


FIGURE 8 Dependence of Ln of the second-order rate constant versus 1/T (Determination of E_{app}), $[\mathrm{MDH}]_0 = 1\ \mathrm{mol\ l^{-1}}$, $[(\mathbf{3})] = 10^{-3}\ \mathrm{mol\ l^{-1}}$.

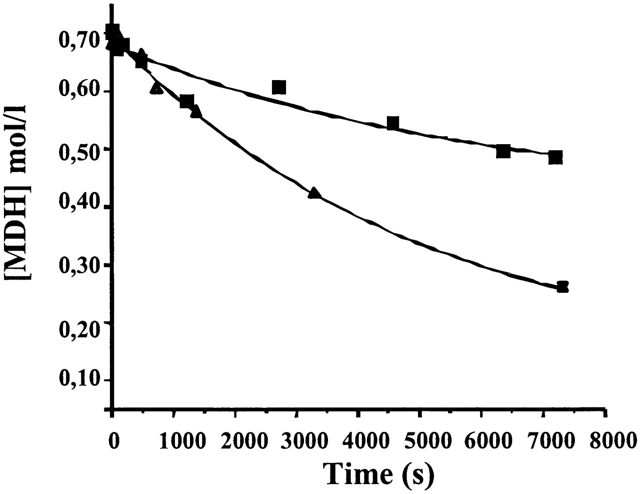


FIGURE 9 Substrate-conversion-time dependences for the condensation of MDH catalysed by (**8**) in toluene at two different temperatures, $[MDH]_0 = 0,7\ mol\ l^{-1}$, $[(8)] = 10^{-3}\ mol\ l^{-1}$, ■ 313 K, ▲ 333 K.

Study of the Catalytic Activity of (8)

An interesting observation is the considerable difference in the catalytic activity of (**3**) compared to (**8**) in which the five chlorine atoms are replaced by phenoxy group. Kinetics of condensation of MDH catalyzed by (**8**) were carried out at two temperatures, 40 and 60°C, with initial concentrations in silanol and catalyst at 0.7 mol l^{-1} and 10^{-3} mol.l^{-1}, respectively. The catalyst (**3**) reacts faster than (**8**) by a factor of about 10, as shown in Figures 9 and 10 and Table III. This decrease in the

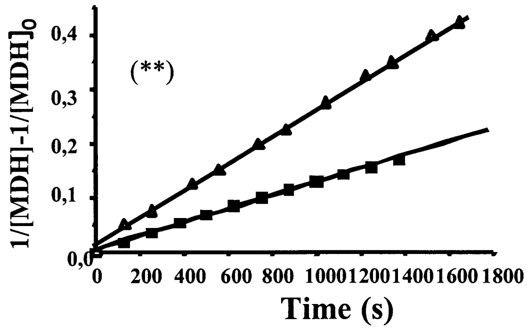


FIGURE 10 Second-order plot for the condensation of MDH in toluene in the presence of (**8**) at a different temperature, $[MDH]_0 = 0.7\ mol\ l^{-1}$, $[(8)] = 10^{-3}$ mol l^{-1}, ■ 313 K, ▲ 333 K.

TABLE III Comparison of Second-Order Rate Constant for the Condensation of MDH Catalyzed by (**8**) at Two Different Temperatures, $[MDH]_0 = 0, 7$ mol l^{-1}, $[(\mathbf{8})] = 10^{-3}$ mol l^{-1}

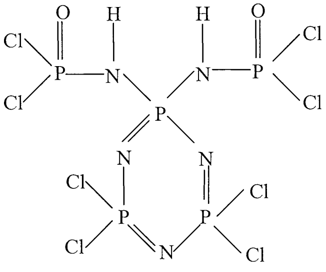
Temperature (K)	K_{app} ($l.mol^{-1}.s^{-1}$)
313	$0.62.10^{-4}$
333	$1.28.10^{-4}$

rate of the MDH condensation reaction may be explained by assuming that the substituted cyclophosphazene compounds (**8**) exhibit only one $-N{=}PCl_3$ group by the bulk effect of the phenoxy groups and also by its lower acidity.

MECHANISM OF THE CONDENSATION PROCESS

All of these results prompted us to investigate in detail the reactivity of the model compound (**3**) towards the linear siloxane oligomers MDH and MD_2M in an attempt to gain more knowledge concerning the siloxane condensation and redistribution and to establish the condensation reaction mechanism of MDH.

To our knowledge, no study concerning the hydrolysis by the liquid water and the action of alcohols (in absence of tertiary amine), on compound (**3**) was published. Lehr[27] showed, however, that the action of two equivalents of formic acid on (**3**) leads to the hydrolysis product (**3″**).



(3")

The ^{31}P NMR spectrum of this compound is characterized by a doublet at $\delta = 21.4$ ppm (PCl_2 intracyclic) ($^2J_{PP} = 46$ Hz), a singulet at $\delta = 0.7$ ppm ($-NH-P(O)Cl_2$), and a multiplet in $\delta = -13.1$ ppm (PN_4). Some authors also studied the substitution of the chlorine atoms in (**3**), (**3″**), and in a compound similar to (**8**) ($N_3P_3(OC_6H_4X)_5$ $N{=}PCl_3$, X = p-OCH_3,[28,29] by reaction of the latter with alcohols (in presence or not of tertiary amine), or with alcohol salts. In the three cases, they indicate the formation of products of types $N_3P_3(OR)_4(N{=}P(OR)_2OH)_2$ and $N_3P_3(OR)_5(N{=}P(OR)_2OH$ and also postulate, on the basis of infrared (IR) spectra, the existence of the equilibrium in Equation (2) between two tautomeric forms.

$$\diagup N{=}\overset{\mathrm{OH}}{\overset{|}{P}}(OR)_2 \rightleftharpoons \diagup\overset{\mathrm{H}}{\overset{|}{N}}-\overset{\mathrm{O}}{\overset{\|}{P}}(OR)_2$$

(2)

The analogy can also be made with the reactivity of P_2NOCl_5 with alcohols[30] (in the presence of an excess of latter), which first leads to $HN(POCl_2)_2$ and then to the esters of imidodiphosphorique acid $HN(PO(OR)_2)_2$.

Another fact that is worth mentioning concerns the highest reactivity of the $-N{=}PCl_3$ group in (**3**) compared to $-NPCl_2$ intracyclic group. Indeed it is possible by reaction of (**3**) with the sodium phenol salt at ambient temperature to synthesize the compound $N_3P_3Cl_4(NP(OC_6H_5)_3)_2$.[31] This should be attributed to the easier ionization of $NPCl_3$ compared to $NPCl_2$.

We approached these results by investigation of the reaction of compound (**3**) with siloxanes in the presence of H_2O, with H_2O alone, and finally with MDH. The reaction in all cases was investigated by a sampling technique. ^{31}P NMR spectroscopic analysis permitted the reaction to be followed directly. For that purpose, three tubes were prepared that contained the following mixtures and that were maintained at ambient temperature (20°C):

tube 1, (**3**)/MD_2M/H_2O/toluene, molar ratio: $[MD_2M]/(\mathbf{3}) = 2$ and $[H_2O]/(\mathbf{3}) = 10$;
tube 2, (**3**)/H_2O/toluene, molar ratio: $(\mathbf{3})/[H_2O] = 1$; and
tube 3, (**3**)/MDH/toluene, molar ratio: $[MDH]/(\mathbf{3}) = 2$.

The evolution of ^{31}P NMR spectra versus time, in the case of tube 1, is represented in Figure 11. The reaction takes place in heterogeneous media (H_2O is miscible neither with toluene nor with MD_2M), so we can expect a slow hydrolysis of (**3**).

Concerning the absence of the reactivity of (**3**) towards MD_2M at ambient temperature, as long as H_2O is not present no evolution of the ^{31}P NMR spectra has been detected. Once H_2O is introduced, the spectrum is characterized first of all by the appearance of four supplementary signals compared to the virgin spectrum of (**3**) (Figure 11a), a doublet

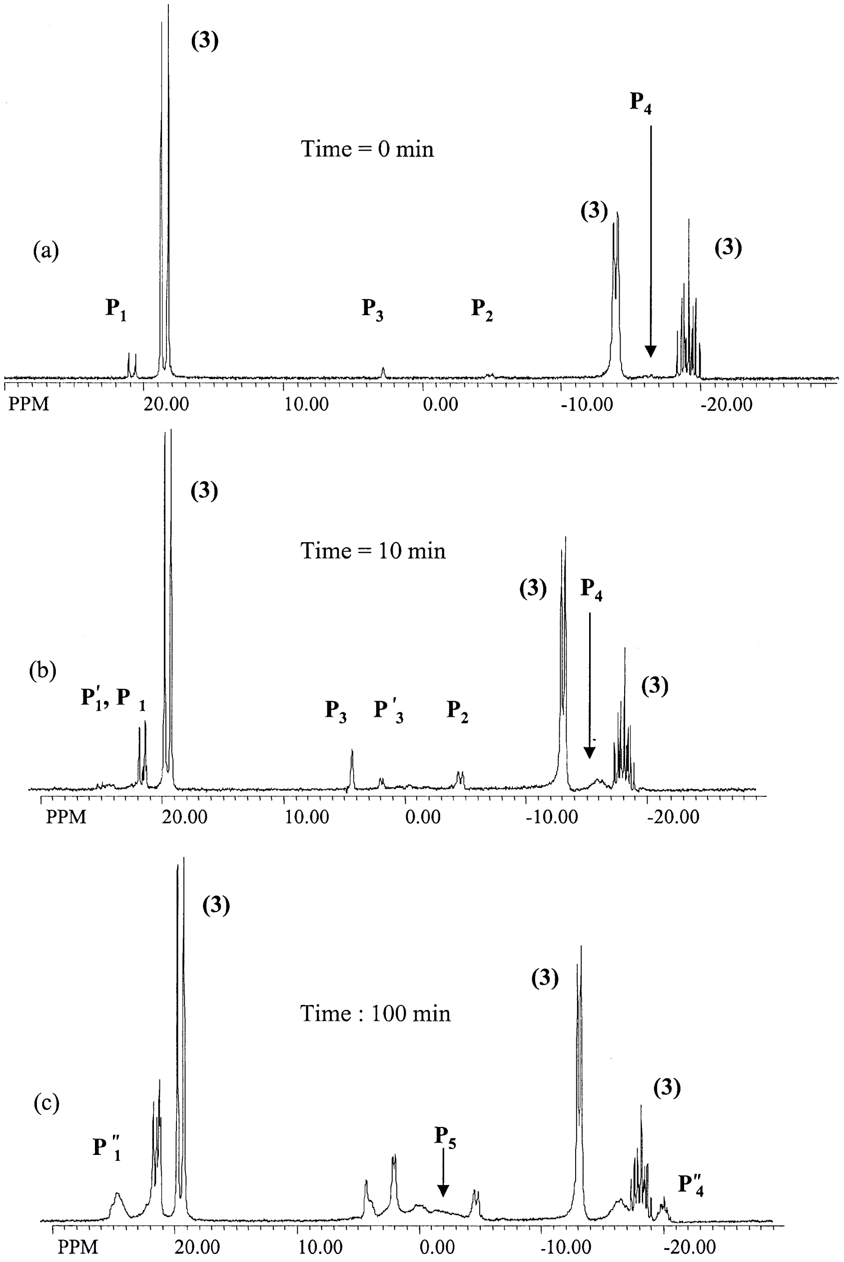
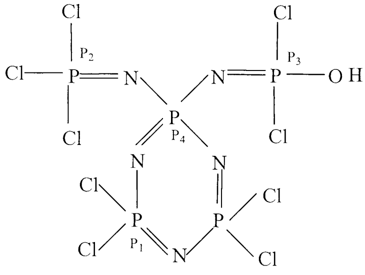


FIGURE 11 ^{31}P NMR proton decoupled spectra of the solution (**3**)/H_2O/ MD_2M/ toluene (tube 1), $[MD_2M]/[(3)] = 2$, $[H_2O]/[(\mathbf{3})] = 10$ at 20°C, (a) 0 min, (b) 10 min, (c) 100 min.

centred at $\delta = 20.8$ ppm ($J = 59$ Hz), a singlet at $\delta = 2.8$ ppm, a doublet at $\delta = -5.6$ ppm ($J = 40.9$ Hz), and a multiplet at $\delta = -17$ ppm. On the basis of the chemical shift and the coupling constants, we can, by comparison to the spectrum of (**3**), attribute the doublet at $\delta = 20.8$ ppm to an phosphor atom (P_1) of intracyclic $NPCl_2$ moiety and that at $\delta = -5.6$ ppm to an phosphor atom (P_2) in exocyclic $-NPCl_3$ group. These results are in accordance with theformation of the monohydrolyzed compound, namely (**3′**), shown below:



(3′)

In that case, the singlet at $\delta = 2.8$ ppm could be attributed to the hydrolyzed $-N{=}PCl_3$ group (P_3), to which two tautomeric forms, $-N{=}PCl_2(OH)$ or $-NH{-}P(O)Cl_2$, correspond. The multiplet at $\delta = -17$ ppm could be then attributed to the intracyclic (P_4) phosphor of PN_4 moiety.

The evolution of ^{31}P NMR spectra versus time is characterized, first of all (Figure 11b) by the appearance of two other doublets of weak intensities, the one (P'_1), overlapping with the doublet corresponding to P_1 centered at $\delta = 20.4$ ppm ($J = 38.3$ Hz), with the other one (P'_3) centered at $\delta = 0.9$ ppm ($J = 22$ Hz). We should note that the sum of the intensities (I_{NPCl3} in (**3**) + I_{P2} + I_{P3} + $I_{P'3}$) is equal to that of the intensities (I_{NPCl2} in (**3**) + I_{P1} + $I_{P'1}$), and equals twice of (I_{PN4} in (**3**) + I_{P4}). The structure of compound (**3**) is well preserved.

Secondly (Figure 11c), with the appearance of a wide signal badly resolved (P''_1), centered at $\delta = 23.7$ ppm, a multiplet P''_4 increases the intensity with that of the doublet (P'_1), of a signal badly resolved at $\delta = -0.8$ ppm (P_5) and finally by a net increase of the doublet at $\delta = 0.9$ ppm (P'_3). The attribution of these signals already mentioned will be done later on in this study.

We compared this evolution to that obtained for the mixture (**3**)/(H_2O) toluene (molar ratio (**3**)/H2O = 1, tube 2). In Figure 12 are represented the ^{31}P NMR spectra of the mixture (**3**)/H_2O/MD_2M/toluene (Figure 12a) and (**3**)/H2O/toluene (Figure 12b) after 30 minutes of

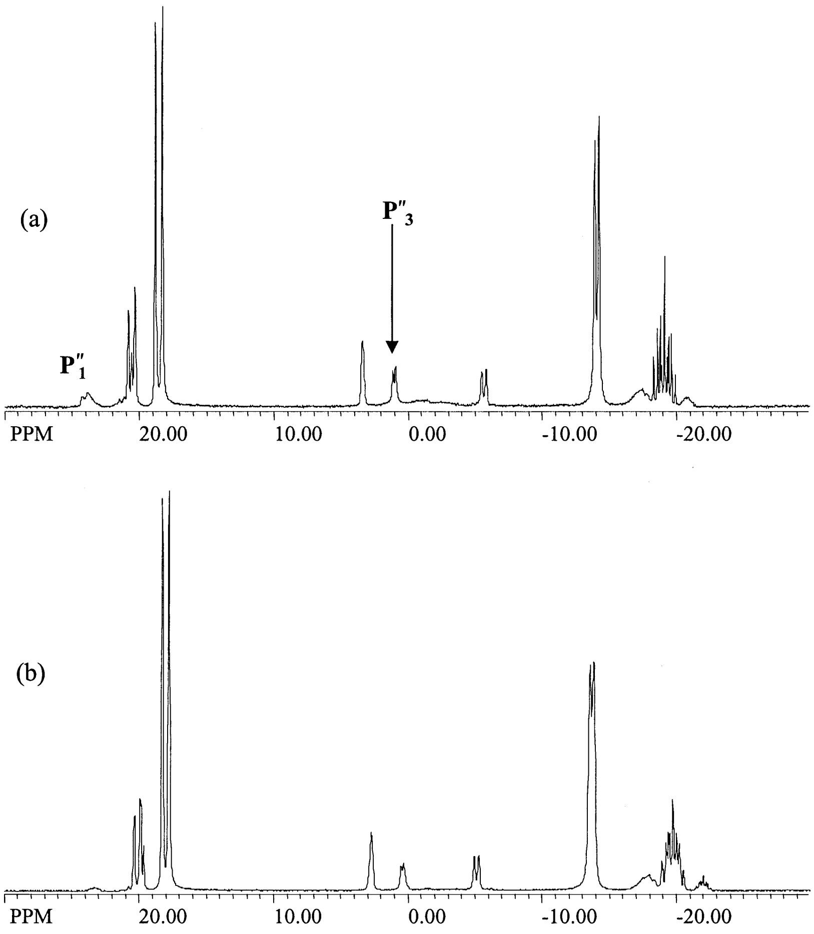


FIGURE 12 ^{31}P NMR proton decoupled spectra of the solution, (a) (**3**)/H_2O/MD_2M/toluene (tube 1) and (b) (**3**)/H_2O/toluene (tube 2) after 30 min of reaction.

reaction. By comparing the two spectra, we can note that they are strictly identical except for the multiplet of (P''_1), which is hardly perceptible. It is necessary to note that in both cases an important precipitate arises in the beginning of the reaction, so the spectra correspond only to the soluble products in the media.

In Figure 13, we have reported the ^{31}P NMR spectrum of compound (**3**) introduced into the mixture of MDH/toluene, (MDH/(**3**) = 2) after 40 min of reaction, (tube 3). In this case, the formation of H_2O resulting from MDH condensation is progressive. From the beginning of the

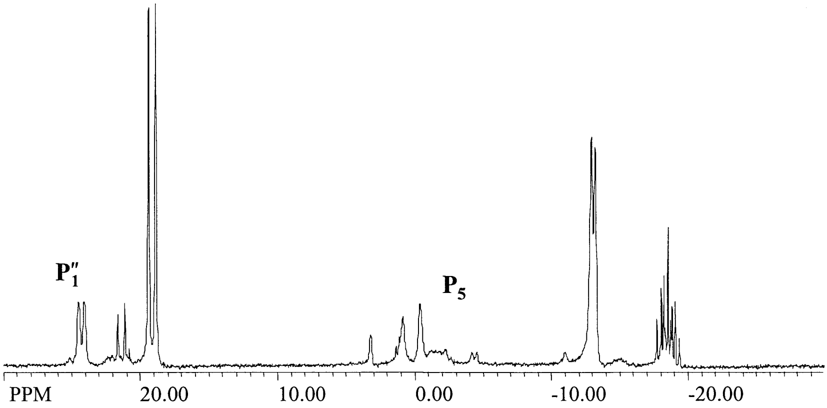
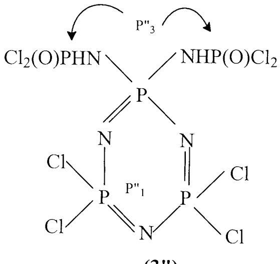


FIGURE 13 ^{31}P NMR proton decoupled spectrum of the solution (**3**)/MDH/toluene (tube 3), [MDH]/[(**3**)] = 2 after 40 min of reaction.

reaction (after 6 min), in addition to the signals already attributed to the monohydrolyzed compound (**3′**), two signals of equal intensity appear, a little perceptible doublet at $\delta = 24.2$ ppm ($J = 49$ Hz) as well as a singlet at $\delta = 0.8$ ppm. These values, compared to those obtained by *Lehr*[26] in the study of the hydrolysis of (**3**) by the formic acid, lead us to attribute the doublet to the intracyclic phosphor $NPCl_2$ (P''_1) and the singlet to the exocyclic phosphor $NHP(O)Cl_2$ (P''_3) in the dihydrolyzed compound (**3″**), below:

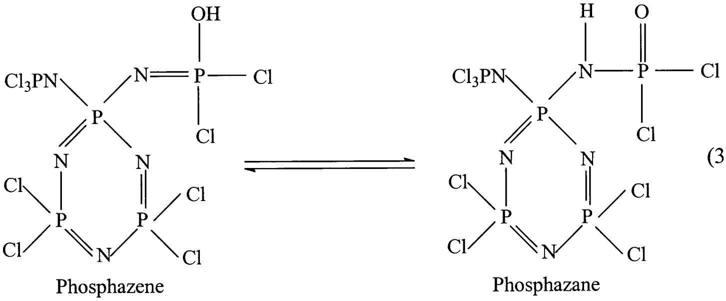


(3'')

We should also note that the signals in the range of the chemical shift $\delta = 1.3$ ppm to $\delta = -4$ ppm change. Indeed, the badly resolved signal which was attributed to P_5 in the case of the mixture (**3**)/MD_2M/H_2O was transformed to a singulet at $\delta = -0.4$ ppm as well as a wide signal centered at $\delta = -2.1$ ppm, the latter becoming more intense. In this domain of chemical shift corresponds to the phosphor atoms of $-P(O)(OH)_nCl_{2-n}$ ($n \neq 0$) or $NHP(O)(OH)_2$ which is in agreement with a supplementary hydrolysis of (**3″**).

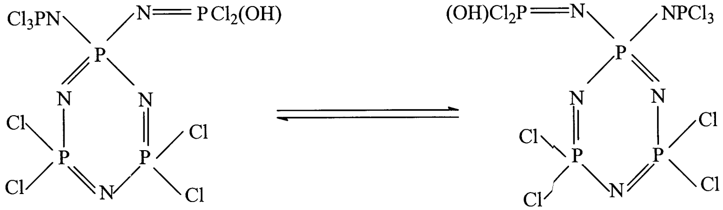
The fact that the sum of the intensities of the signals in the range of $\delta = 3.1$ and $\delta = -4,5$ ppm becomes superior to that corresponding to $P_1 + P'_1 + P''_1$ shows that the structure of type (**3″**) is not preserved anymore. This could be due to the cleavage of the exocyclic NP bonds. In this case, the precipitate is less important compared to the previous experiments. In this study we note that even after 75 min of reaction, 55% of the phosphor atoms associated to the initial compound (**3**) still remain in solution.

The presence of the doublets of equal intensities at $\delta = 20.4$ ppm and $\delta = 0.9$ ppm (P'_1 and P'_3, Figures 11b and 12), in the case of the hydrolysis of compound (**3**) in MD_2M and toluene or only in toluene, can be explained by an equilibrium between two tautomeric phosphazene–phosphazane forms according to the reaction in Equation (3).



(3)

Then, in the phosphazane form (for the exocyclic phosphor atoms) the doublet would correspond at $\delta = -5.6$ ppm ($NPCl_3$) and the singlet at $\delta = 2.8$ ppm ($-NHP(O)Cl_2$), and in the phosphazene form the doublet would correspond at $\delta = 0.9$ ppm. The uniqueness of this last signal can be explained by a reversible and fast migration of the hydroxyl group between the exocyclic phosphor atoms according to the reaction in Equation (4).



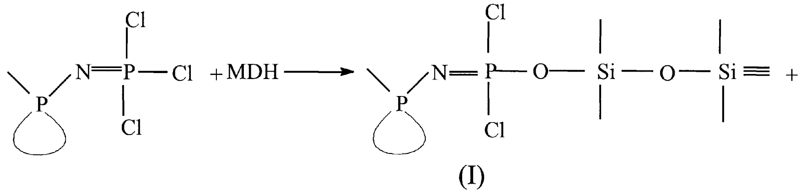
(4)

This migration was already reported by Kabachnik et al.,[32] in the case of the silylated monophosphazene compounds above −30°C according to the reaction in Equation (5).

$$R_2(Me_3SiO)P_a{=}N{-}P_b(O)R_2 \rightleftharpoons R_2P_a(O){-}N{=}P_b(OSiMe_3)R_2$$

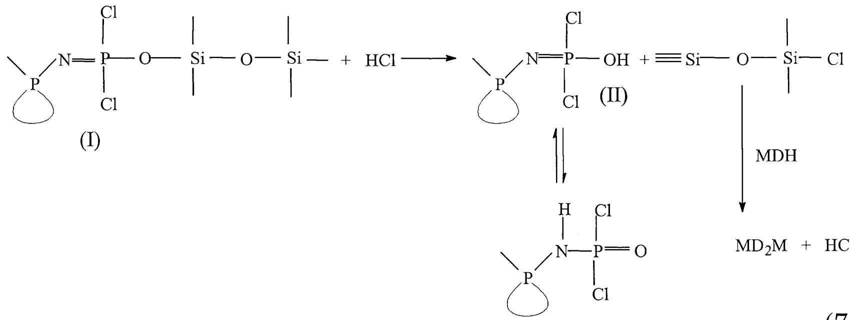
$$R = CH_3, C_2H_5 \qquad (5)$$

However, this phenomenon is quasi nonexistent in the case of the reaction of (**3**) with MDH. Indeed, only the hydrolysis products of (**3**), namely (**3′**) and (**3″**), were formed. (the analogy can be made with the reaction of $Cl_3PNP(O)Cl_2$ with MDH[20,21]). The formation of such compounds can be explained by the succession of the reactions in Equations (8)–(10). The first step consists in the formation of the silylated intermediate of type (I), according to the reaction in Equation (6):

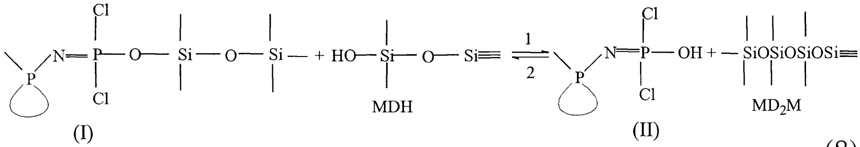


(6)

The immediate passage to the hydroxylated form (II) can be made by the action of HCl on (I) followed by the cleavage of P—O—Si bond according to the reaction in Equation (7) and by a desilylation reaction, similar to that of the silylated esters of the imidodiphosphoric acid with alcohols in excess,[32] which in our case led to the intermediate (II) according to Equation (8), the reaction in the right direction 1 being faster:

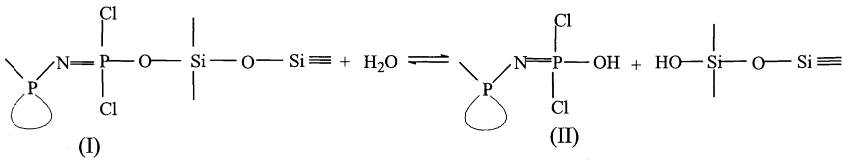


(7)



(8)

We can also think out the reaction of H_2O with (I) according to Equation (9):

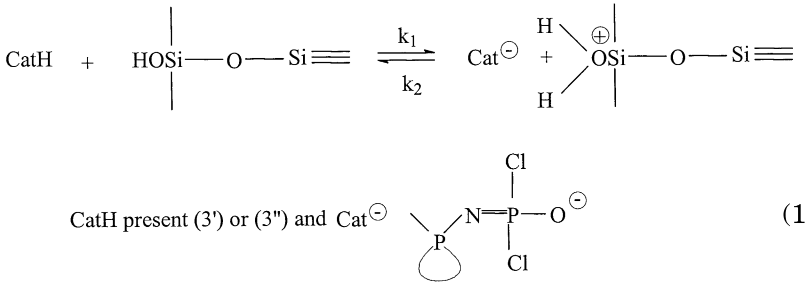


(9)

This reaction must, however, be less important in the beginning of condensation, a period in which the concentration of H_2O is weak with regard to that of the MDH.

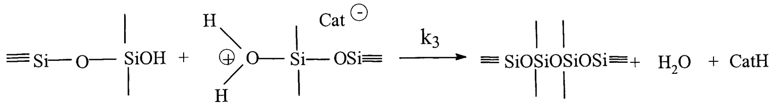
The reactions in Equations (6)–(8) can be considered as initiation reactions for the MDH condensation. The active entities could be the hydroxylated compounds (**3**) and (**3′**), (whose concentration should be proportional to compound (**3**)), associated to the released HCl, which can also play a role but, as has been shown, alone could not explain the kinetics of the condensation reaction.

According to the mechanism proposed to explain the acid catalysis of the polycondensation of silanols, it is then logical to suppose the formation of an oxonium ion from (**3**) and (**3′**) according to the reaction in Equation (10).



(10)

Followed by the reaction of the silanol on this ion according to the reaction in Equation (11).



$$\equiv Si-O-SiOH + \overset{H}{\underset{H}{\oplus O}}-Si-OSi\equiv \; Cat^{\ominus} \xrightarrow{k_3} \equiv SiOSiOSiOSi\equiv + H_2O + CatH$$

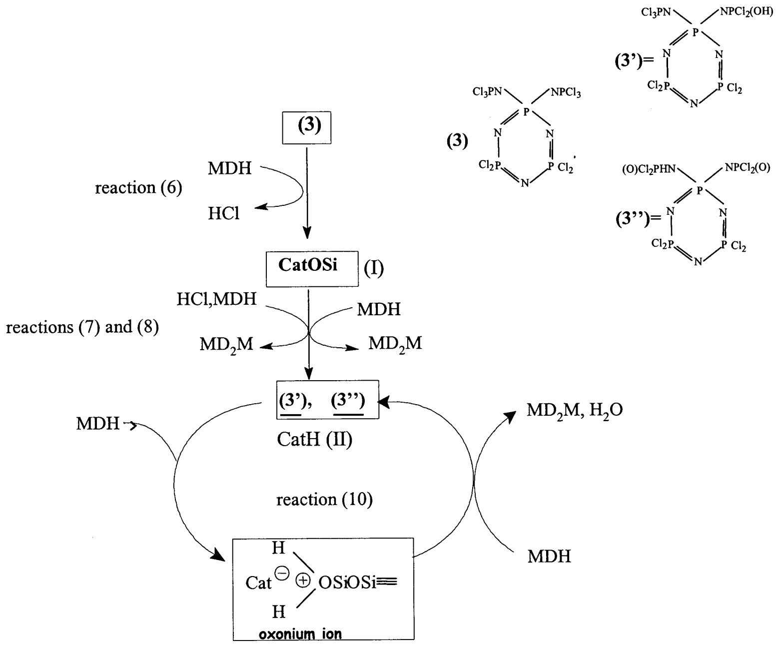
(11)

So, the order 1 with regard to the catalyst can be explained by the fact that the protonated form (CatH) is present in a quickly reached equilibrium, which does not determine the rate of the condensation reaction.

So, the concentration of the oxonium ions is proportional to CatH—in our case to (**3**). Therefore, the rate of the condensation reaction which is imposed by the reaction in Equation (11) is second order in MDH according to

$$V = \frac{k_3 k_1}{k_2} \times \frac{[\mathrm{catH}][\mathrm{MDH}]^2}{[\mathrm{cat}^-]}$$

Everything that precedes brings us to suggest the reactional mechanism of Scheme 2.



SCHEME 2

EXPERIMENTAL SECTION

Chemicals

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

Compounds used for the determination of response factors in gas chromatography, i.e., $Me_3Si[OSiMe_2]_n$-$OSiMe_3$, n = 0, 1, 2, and

Me_3SiOH, were obtained and purified using well-known procedures. Their purities determined by gas chromatography were at least 99%.

All experiments were carried out under an atmosphere of dry oxygen-free nitrogen. Solvents were dried over molecular sieves and distilled prior to use. The preparation of different cyclic phosphazenes compounds (**2**)–(**8**), have been performed according to the different literature: (**2**);[27–33] (**3**);[34] (**4**) and (**5**);[35] (**6**);[36] (**7**);[27] and (**8**).[28]

Kinetics 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 dry nitrogen and charged with the required amounts of solvent, standard for gas chromatography (dodecane), and substrates by means of precision Hamilton syringes, keeping a stream of dry nitrogen through the stopcock. The reactor was thermostated by Maton TH30 thermostat, keeping the temperature constant within ±0.1°C. The zero sample was withdrawn by means of a 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 a quenching agent (i.e., 20 μl of ET_3N). Samples were then subjected to gas chromatography analysis.

Gas Chromatography

Gas choromatography analyses were performed with a Shimadzu GC-14A gas chromatograph working with Shimadzu CR-4A integrator. The chromatograph was fitted with a flame ionization detector, semi-capillary column CPSIL 5CB ($l = 30$ m, $d = 0.53$ mm), temperature 50–280°C, programmed 10°C min^{-1}. Detector and injector temperatures were 300°C. Dodecane was used as internal standard.

NMR Spectroscopy

^{31}P NMR analysis were made with a Bruker 300 WP instrument, working at 121.49 MHz frequency.

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