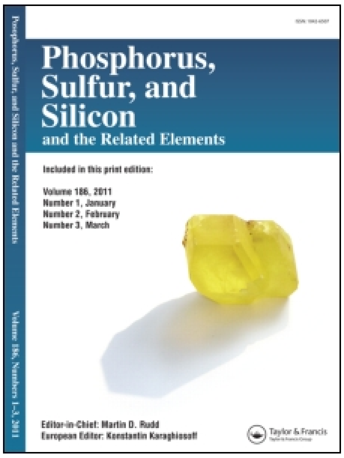

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# KINETICS AND MECHANISM OF THE REACTION BETWEEN OLIGOSILOXANES AND P-TRICHLORO-N-DICHLOROPHOSPHORYL MONOPHOSPHAZENE ($Cl_3P{=}N{-}POCl_2$)

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# KINETICS AND MECHANISM OF THE REACTION BETWEEN OLIGOSILOXANES AND P-TRICHLORO-N-DICHLOROPHOSPHORYL MONOPHOSPHAZENE ($Cl_3P=N-POCl_2$)

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$^{31}P$ NMR investigation has been made of the action of $Cl_3P=N-POCl_2$ (I) first on hexamethyldisiloxane $(Me_3Si)_2O$ and then on oligosiloxanes $Me_3Si-(OSiMe_2)_n-OSiMe_3$ n = 2 and n=3. The reactions were carried out in bulk or in solution with molar ratios siloxane/(I) varying from 1 to 5. It was demonstrated 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 $Cl_2OP-N=PCl_2O-(SiMe_2-O)_nSiMe_3$ (II). For n=2, 3 the siloxane redistribution reactions were observed by $^{29}Si$ NMR analysis. A two steps 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, arising from the solvatation by the siloxane of this phosphazenium ion and /or of (II) leading to the redistribution reactions. The influences of the solvent, of trimethylchlorosilane, of the temperature, and of the addition of a protonated species (MDH) were investigated.

*Keywords:* Chlorophosphazenes; Siloxane; Redistribution; Reactivity; Mechanism

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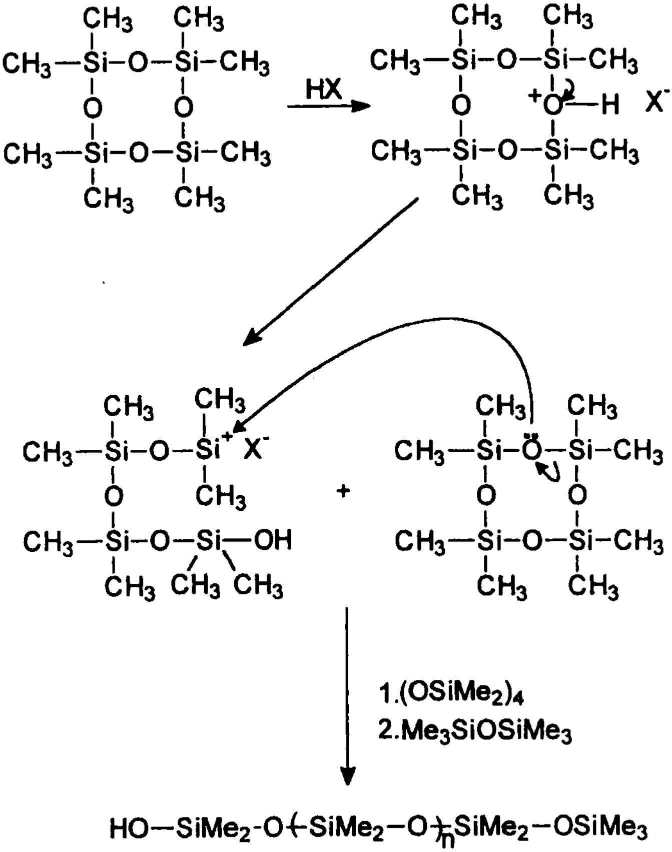
* Corresponding Author.

## INTRODUCTION

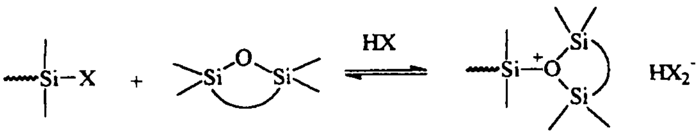
The polar nature of the siloxane bond makes it susceptible to attack by acids and bases, and a number of studies devoted to the acid and base catalysed polymerization of cyclosiloxanes have been reported[1-3].

In the cationic process, initiated by a protonic acid, it is generally agreed that $H^+$ protonates a ring oxygen of a cyclosiloxane and that subsequent Si-O bond cleavage forms a silicon cation which attacks another siloxane ring oxygen and continues the polymerization process according to reaction (1).



(1)

However, the occurrence of a silylenium ion is controversial, and it is usually postulated that the active propagating center is an oxonium ion, which can be generated according to reactions (2)[4] (3)[5], (4)[6,7].



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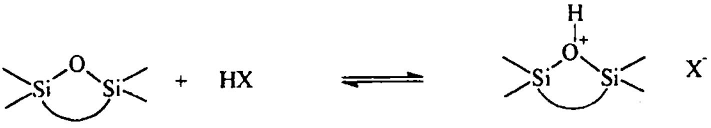
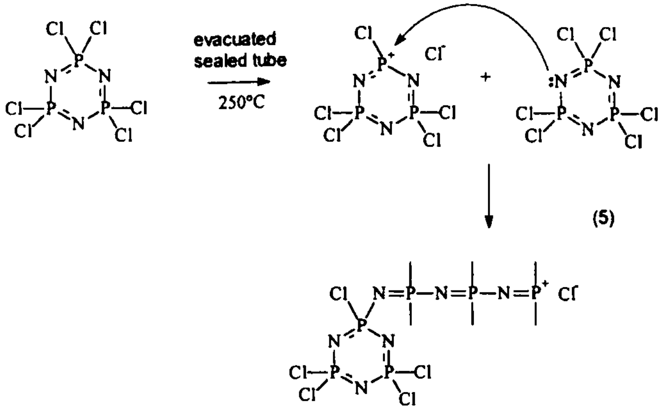


(4)

A similarity exists between this mechanism and the one of chlorocyclophosphazenes polymerization which is believed to involve an initial ionization of a P-Cl bond, producing a phosphazenium cation, which reacts at the lone pair electrons of the nitrogen atom of another phosphazene ring, initiating the polymerization reaction (5)[8,9].



(5)

That similarity prompted Allcock *et al.* to investigate the reaction between hexachlorocyclotriphosphazene $(N{=}PCl_2)_3$ and hexamethylcyclotrisiloxane $(Me_2SiO)_3$ with the aim to generate hybrid siloxane-phosphazene species[10]

In that study, it was reported that the cothermolysis of these compounds resulted in a product mixture including the higher silicone rings $(Me_2SiO)_{4-6}$ produced by siloxane ring-ring equilibration.

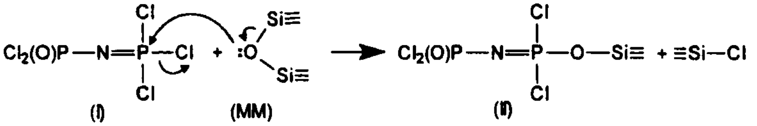
It was also reported by *Chojnowski et al.*[11] and *Hager et al.*[12] that the oligophosphazenium salts $[Cl_3P(\text{-}N{=}PCl_2)_n\text{-}Cl]^+ X^-$, X=Cl, $PCl_6$, $SbCl_6$, $AlCl_4$ and neutral phosphoryl phosphazenes $Cl\text{-}(Cl_2P{=}N)_n\text{-}POCl_2$, $HO\text{-}(Cl_2P{=}N)_n\text{-}POCl_2$ (n=1, 2,...) were efficient catalysts of silanol polycondensation and linear polysiloxanes rearrangement respectively[11,12].

It was particularly postulated that the catalysis of the oligosiloxanes redistribution with the phosphazenium salt $[Cl_3P{=}N\text{-}PCl_3]^+$ $SbCl_6^-$ proceeded with the mediation of protic species (traces of water or silanol) producing the protonated active center $Me_3SiO(Me_2SiO)_nCl_2P^+\text{-}NH\text{-}POCl_2$[12].

All these results, prompted us to investigate in details, the reactivity of the model compound P-trichloro-N-dichlorophosphoryl monophosphazene $Cl_3P{=}N\text{-}POCl_2$ (I) towards the linear siloxanes $Me_3Si\text{-}(O\text{-}SiMe_2)_n\text{-}OSiMe_3$ ($MD_nM$ n=0, 2, 3) in an attempt to gain more knowledge concerning the siloxanes redistribution mechanism. Indeed, although the report that compounds $(Cl_2OP)_2N\text{-}Si(CH_3)_3$ and $Cl_2OP\text{-}(N{=}PCl_2)_x\text{-}N{=}PCl_2OSi(CH_3)_3$, x=1, 2 were believed to be formed by reaction between (I) or $Cl_2(O)P\text{-}(N{=}PCl_2)_x\text{-}N{=}PCl_3$and a large excess of hexamethyldisiloxane (based on $^{31}P$ NMR data)[11,12], yet the title reaction does not seems to have been studied in details.

## RESULTS AND DISCUSSION

It has been anticipated that the reaction of (I) with MM would occur with simultaneous formation of (II) and trimethylchlorosilane according to reaction (6)[11,12].



(6)

Indeed, in view of molecular stability ratios calculations[13], and of the reactivity of (I) towards O-nucleophiles, MM is the attacking reagent which brings an electron pair to the -N=$PCl_3$ phosphorus atom inducing cleavage of the Si-O-Si bond and elimination of $Me_3SiCl$.

In a first step, the reaction was performed in toluene at 60 °C with a molar ratio 1/1. The resultant products were analysed by $^{31}P$ and $^{29}Si$ NMR spectroscopy.

In the two cases, $^{31}P$ NMR spectra showed only one singlet at $\delta = -9.1$ ppm and $^{29}Si$ NMR spectra only two singlets with the same integrals at $\delta = 37.6$ ppm and $\delta = 30.2$ ppm (figure 1). These signals can be attributed to the phosphorus atoms in (II), and to the silicon atoms in (II) and $Me_3SiCl$ respectively.

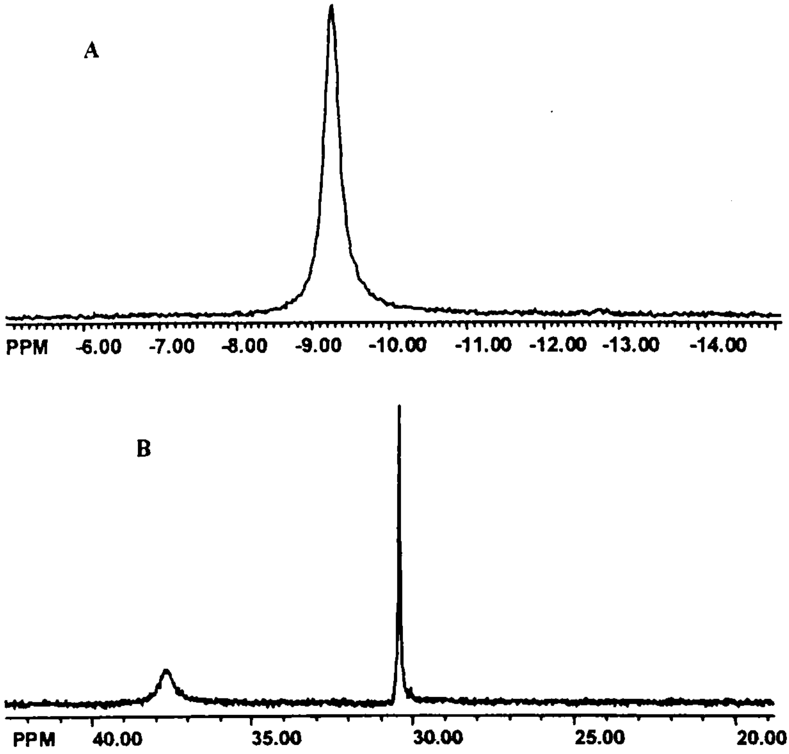
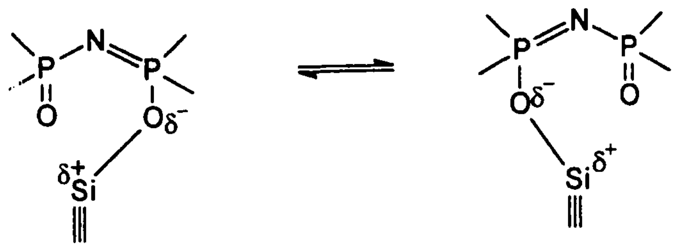


FIGURE 1 $^{31}P$ (A) and $^{29}Si$ (B) NMR spectra of the reaction of (I) with MM. Solvent toluene, molar ratio 1:1, temperature 60 °C, duration 115 h

These results are in accordance with those of *Roesky et al.*[14] for the same compound synthesized from sodium tetrachloroimidodiphosphate $NaN(POCl_2)_2$ and $Me_3SiCl$. The fact that only one singlet appears in $^{31}P$ NMR and the broadening of the signal of (II) in $^{29}Si$ NMR show that the two phosphorus atoms are magnetically equivalent due to the reversible exchange of the trimethylsilyl group between the two oxygen atoms, equation (7)[14].



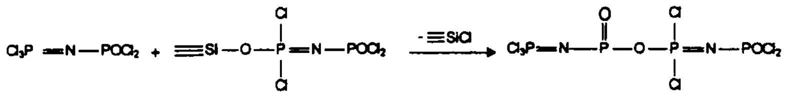
(7)

A similar $^{31}P$ NMR spectrum was obtained for higher MM / (I) molar ratios. The formation of (II) was also confirmed by the IR spectrum of the reaction product (molar ratio MM/(I) = 1) which after elimination of $Me_3SiCl$, contains absorption bands at 1257, 843 and 767 $cm^{-1}$ characteristic of the trimethylsilyl group, at 1110, 965 $cm^{-1}$ ascribable to the P-O-Si group[15], at 1320 $cm^{-1}$ representative of the P=N valence vibration; the Si-O-Si absorption band (at 1049 $cm^{-1}$ in MM) being absent from spectrum.

Leading to the complete conversion of (I) into (II), the reaction can be considered to be irreversible, and the only monosubstitution may result from electron supply from the $OSiMe_3$group to the phosphorus atom which lowers the reactivity of a $PCl_2OSiMe_3$ unit below that of a $PCl_3$ unit.

The use of temperatures higher than 60 °C (70–100°C), resulted in undesired condensation reactions when the conversion of (I) exceeded 60%. These reactions were characterized by the first appearance in the $^{31}P$ NMR spectra of signals at $\delta = -23$ ppm (dd), $\delta = -14$ ppm (t), $\delta = 6$ ppm (d) and of a signal near $\delta = -12$ ppm partly overlapped by the one of the $POCl_2$ unit in (I). All coupling constants were in the order $J \approx 41$ Hz.

According to the results obtained by *D'Halluin et al.*[16] for the reaction between the bis(dichlorophosphoryl)imide $HN(POCl_2)_2$and (I), these signals can be attributed to the compound resulting of the condensation, reaction (8).



$$Cl_3P{=}N{-}POCl_2 + {\equiv}Si{-}O{-}\overset{Cl}{\underset{Cl}{P}}{=}N{-}POCl_2 \xrightarrow{-{\equiv}SiCl} Cl_3P{=}N{-}\overset{O}{\overset{\|}{P}}{-}O{-}\overset{Cl}{\underset{Cl}{P}}{=}N{-}POCl_2$$

(8)

The kinetics of the reactions, carried out in toluene at 70 °C (to reduce their duration) with a molar ratio (I) / MM =1, were followed by $^{31}P$ NMR. The percent conversion was limited to 60% to avoid the condensation reactions. The spectrum of a sample taken at 50% conversion is represented in figure (2).

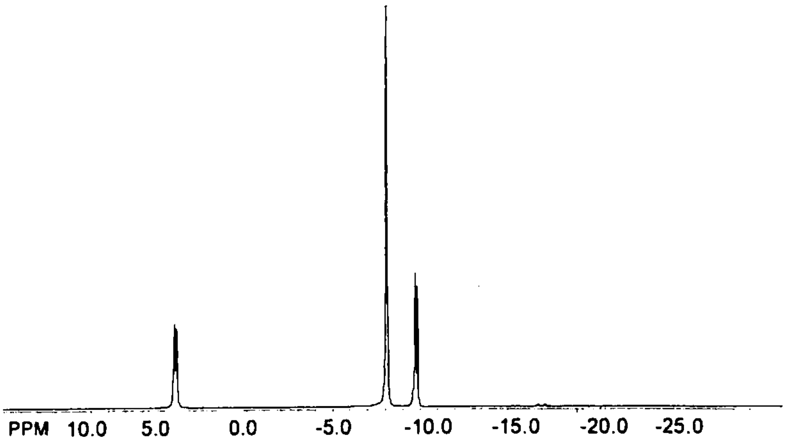


FIGURE 2 Reaction of (I) with MM. Solvent toluene. Molar ratio 1:1, temperature 70 °C $^{31}P$ NMR spectrum of a sample taken at 50% conversion

The disappearance of one molecule of (I) results in the formation of one molecule of (II), therefore the ratio R= Int (I) / Int (I+II), (where Int (X) represents the integration of signals representative of (I) [$\delta$= 3.0 ppm (d) ($PCl_3$), $\delta$= −10.8 ppm (d) ($POCl_2$)] and (II) [$\delta$=-9.1 ppm]) gives the residual percentage of (I %) at any time. Its variations as a function of time are plotted in figure 3A.

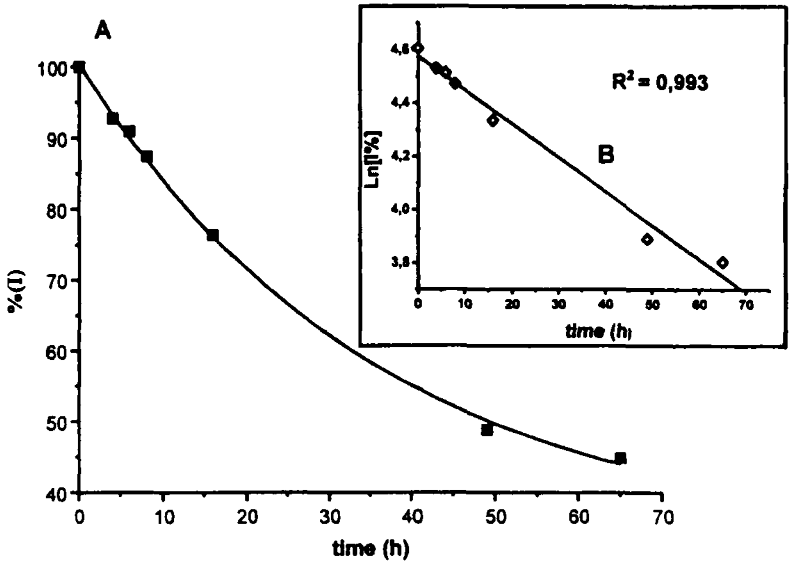


FIGURE 3 Reaction of (I) with MM. Solvent toluene. Molar ratio 1:1, temperature 70 °C. [I] = [MM] = 2.2 mol.l$^{-1}$ A: Evolution of the remaining (I) versus time. B: Kinetics of disappearance of (I)

The reaction is effectively slow, since after about 50 hr only 50 % of (I) have reacted. Since the molecular ratio of the reactants equals one, the rate law disappearance of (I) is:

$$v = -\frac{d[I]}{dt} = k[I]^{\alpha}[MM]^{\beta} = k[I]^{\alpha+\beta}$$

Where $\alpha + \beta$ represents the global order of the reaction.

Plots of In[I %] versus time are linear according to an one-order kinetic law and the rate constant is $k = 3.10^{-6}$ sec$^{-1}$, (figure 3B).

Therefore, the reaction seems to comply with a $SN_1$ type mechanism consisting in two steps, the first being a slow ionization of (I) and rate determining step, and the second being a rapid reaction between the intermediate phosphazenium cation and the nucleophile MM. Reactions (9) and (10).

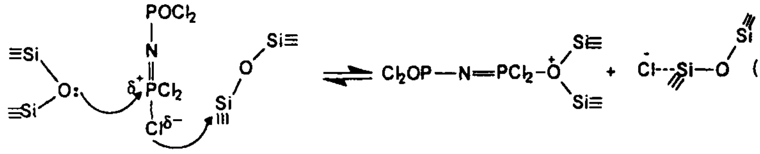
$$Cl_2OP{-}N{=}PCl_3 \xrightleftharpoons{\text{slow}} Cl_2OP{-}N{=}\overset{+}{P}Cl_2\text{-----}\overset{-}{Cl} \qquad (9)$$

$$Cl_2OP{-}N{=}\overset{+}{P}Cl_2\cdots\cdots\overset{-}{Cl} + MM \xrightarrow{fast} Cl_2OP{-}N{=}PCl_2OSi{\equiv} + Me_3SiCl \qquad (10)$$

If the mechanism operates as shown with reactions (9) and (10), the rate should be the same with the other siloxanes $MD_2M$ and $MD_3M$ under the same conditions. Therefore, the kinetics of the reaction of (I) with the three siloxanes $MD_nM$, n=0, 2, 3 were compared in experiments carried out at 70°C with a molar ratio $MD_nM$ / (I) =2 and a conversion limited to 60 %.

As expected plots of (I %) and ln(I %) versus time were superposable with an apparent rate constant $k = 7.10^{-6}$ $sec^{-1}$.

Since the slow step involves only (I), the rate should be dependent only on its concentration. However, the Si-O bond in siloxane being partially polarized, this last may act as an electron pair donor (EPD) as well an electron pair acceptor (EPA) solvent and the polarization of the P-Cl bond to be ionized can occur via nucleophilic and electrophilic attack of the siloxane on the electropositive phosphorus and electronegative chlorine atoms respectively. Reaction (11).



(11)

Thus, the use of siloxane at once as reactant and solvent (solvolyse) should influence (increase) the rate of the reaction. The following examples are illustrative. Three reactions between $MD_2M$ and (I) were performed with the molar ratios $MD_2M$ / (I) = 1, 2 and 5 The apparent rate constants were k= $3.10^{-6}$, $7.10^{-6}$, $2.1\ 10^{-5}$ $sec^{-1}$ respectively. These results show that the siloxane effectively acts as an ionizing medium.

If a such ionization is admitted, it is obvious that catalysis of the oligosiloxane $MD_nM$ redistribution reactions with (I) should be possible.

To confirm that, the $^{29}Si$ NMR spectra of the products obtained by reaction of (I) with $MD_nM$, n = 2, 3 (molar ratio $MD_nM$ / (I) = 1 temperature

60°C) within the NMR tube (to provide against hydrolysis), have been carried out. As an example the one with $MD_2M$ was reported in figure (4). In each case, the spectra recorded after complete reaction (checked by $^{31}P$ NMR) showed four singlets at $\delta = 37.6, 30, 7, -19.2$ ppm and a multiplet at $\delta = -21.6$ ppm which are characteristic of the silicon atoms in P-O-Si≡ groups, $Me_3SiCl$, M terminating units, cyclic species $D_4$( also identified by gas chromatography) and D units (including D in higher cyclic siloxanes) respectively[17]. No $M^{Cl}$ units were detected.

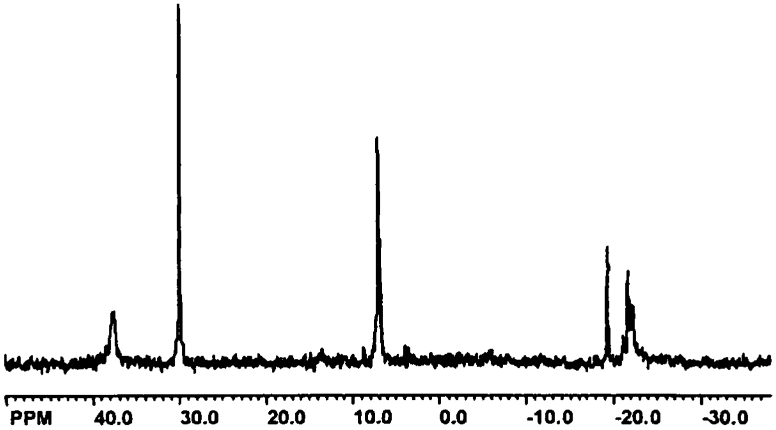
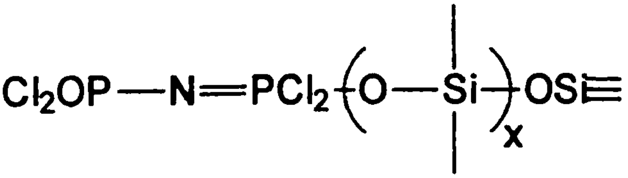


FIGURE 4 $^{29}Si$ NMR spectrum of the product of the reaction of (I) with $MD_2M$ in bulk $[I] = [MD_2M] = 1.7$ mol.l$^{-1}$, temperature 60°C

A quantitative evaluation was also made of the amount of the silicon atoms in each of these species (obtained by use of chrome III acethylacetonate as relaxation reagent, or with a long relaxation delay). The results indicated that the ratios between the D ($\delta = 21.6$ ppm) and M units ($\delta = 7$ ppm) (excluding P-O-Si≡) which should be 2 ($MD_2M$) and 3 ($MD_3M$) for a type (6) reaction, were 5.6 and 4 respectively. The variations of these ratios, were also characterized in Infrared spectroscopy by a broadening of the Si-O-Si bands at 1032 and 1069 cm$^{-1}$ in $MD_2M$. (They were found at 1022 and 1079 cm$^{-1}$ in the product of the reaction of (I) with $MD_2M$).

These results associated with the initial 1:1 ratio, the completion of the monosubstitution reaction, the formation of the trimethylsilylderivative $Cl_2OPNPCl_2OSi\equiv$ (II) and of cyclic species, proved in one hand, the occurrence of the $MD_nM$ redistribution, on the other hand the formation of the phosphazenes (III) with $\bar{x} \neq n$.



$$Cl_2OP-N=PCl_2\left(O-\overset{|}{\underset{|}{Si}}\right)_x OSi\equiv \qquad (III)$$

Various factors can affect both the kinetics of the substitution and oligosiloxane redistribution reactions.

We have successively studied the influences of the solvent, of the presence of trimethylchlorosilane, of the temperature and of the addition of a protonated species.

### Influence of the solvent

The nature of the solvent can affect not only the rate, but also the mechanism of nucleophilic substitution reactions. Its ability to transform a covalent bond into an ionic bond, mainly depends on its ability to function as an electron pair acceptor (EPA solvent), or donor (EPD solvent), rather on its dielectric constant.

Acetonitrile which is compatible with (I) and oligosiloxanes and which mainly acts as a dissociating medium (high dielectric constant), but lacks EPA properties, was chosen. Then, a reaction between $MD_2M$ and (I) in acetonitrile was performed with the molar ratios $MD_2M$ /(I)/ $CH_3CN$ = 1/1/4 to compare its kinetics with the former reaction in bulk between $MD_2M$ and (I) in the molar ratio $MD_2M$ / (I) = 5. The temperature was 70 °C in the two cases. It was found that its use caused an approximately 5 fold rate decrease, the global order remaining the same ($k = 4.4\ 10^{-6}\ sec^{-1}$). These results show at once the effect of a solvent change, and that the siloxane effectively acts as a better ionizing medium compared with acetonitrile.

### Influence of trimethylchlorosilane

In order to check its possible effect on the siloxane redistribution reaction, $Me_3SiCl$ was introduced in $MD_2M$ ( $10^{-3}$ mol in $10^{-3}$ mol $MD_2M$). After keeping of this solution at 50 °C during 7 h, it was analysed by gas chromatography. Any $MD_2M$ redistribution products were detected. This result indicated any specific effect of $Me_3SiCl$ on the redistribution reaction.

### Influence of the temperature

A series of three reactions between $MD_2M$ and (I) in toluene (molar ratio 1:1) were performed at three different temperatures 50, 70 and 100 °C.

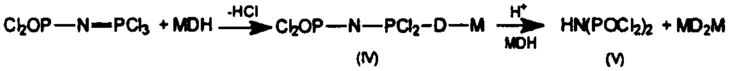
In each case, the rate was measured. We found $k = 1.1\ 10^{-6}$, $3.10^{-6}$ and $1.8\ 10^{-5}\ s^{-1}$ respectively. A plot of lnk against 1/T allowed the calculation of the Arrhenius activation energy of the reaction which was found to be $E_a = 11.1$ Kcal.mol$^{-1}$.

### Influence of the addition of a protonated species

*Chojnowski et al.*[11] have shown that the addition of protonated species had considerable effect on the kinetics of the $MD_2M$ redistribution, (acceleration of the rate and suppression of an induction period). Thus, it was interesting to test the effect of the introduction of a such species, the 1,1,3,3,3 pentamethyldisiloxane -1-ol (MDH), on the reaction system $MD_2M$-(I).

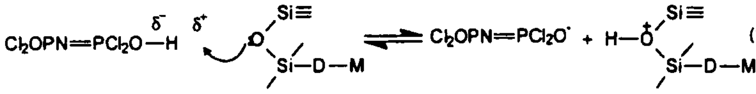
The reaction was performed at 50 °C with molar ratios (I) / $MD_2M$ / MDH = $1/1/3.10^{-2}$. The comparison of the kinetic features of the substitution of (I) with and without MDH showed that the addition of MDH increased the initial reaction rate by a factor of about 3.5, and promoted a change of the kinetic law which in this case don't comply with the one order.

By analogy with the reactions of (I) with alcohols[18], the main factor responsible for the change of the kinetics consists in the reaction of MDH with (I) which leads to the di(dichlorophosphoryl)imide $HN(P(O)Cl_2)_2$ (V) by the way of the O-silylated intermediate (IV) according to the reaction (12), which occurs faster compared with the ionization of (I) (9).



$$\underset{}{Cl_2OP{-}N{=}PCl_3} + MDH \xrightarrow{-HCl} \underset{(IV)}{Cl_2OP{-}N{-}PCl_2{-}D{-}M} \xrightarrow[MDH]{H^+} \underset{(V)}{HN(POCl_2)_2} + MD_2M \qquad (12)$$

The position in $^{31}$P NMR of the signal of (V) in $MD_2M$ was found at $\delta = -6.4$ ppm value which is also consistent with a partial ionization according to reaction (13). Just in comparison, this signal was found at $\delta = +0.1$ ppm in $CCl_4$.



(13)

It can be noted here, that a series of reactions between (I) and $MD_2M$ performed with the same molar ratio (1/1) at the same temperature (70 °C) have given rate constants which were very close to each other (from $k = 3.0\ 10^{-6}\ s^{-1}$ to $3.6\ 10^{-6}\ s^{-1}$). Therefore, a possible hydrolysis of (I) which should lead to the (dichlorophosphoryl) imide $HN(P(O)Cl_2)_2$ (V)[19] can be excluded.

## Overall Reaction Pattern

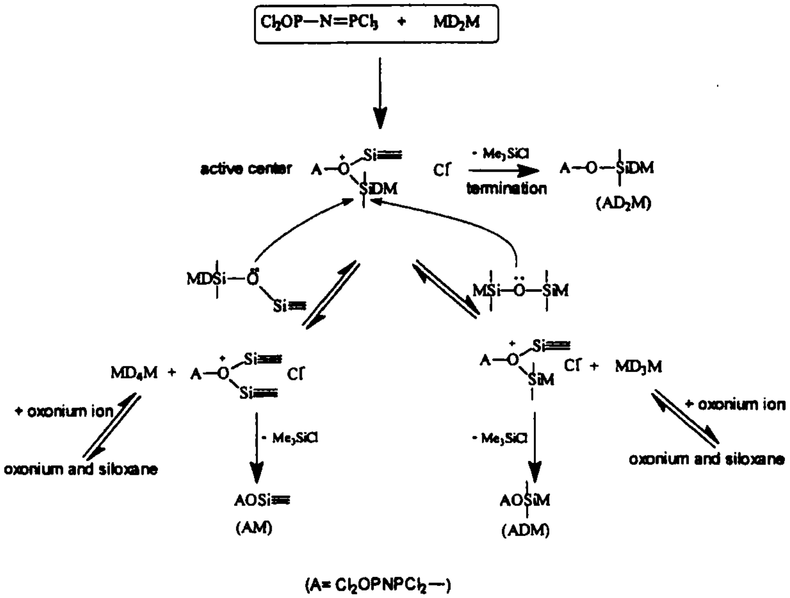
Considering the previous results, and by analogy with the cationic polymerization of cyclosiloxanes or cyclic ethers (ex. THF) it was logical to think that the initiation of the reaction of (I) with $MD_nM$ requires the formation of an oxonium ion in order for the redistribution to take place.

This species can be formed at once from (I) and from (II).

In the first case (from (I) ), initiation should result from reaction (11) leading to the formation of a phosphazene oxonium ion. Then, redistribution should occur via a nucleophilic attack by a siloxane oxygen atom on a silicon $\alpha$ to the oxygen of this ion, leading to the formation of a new siloxane and oxonium ion. This mechanism is represented in scheme 1 in the case of $MD_2M$ redistribution.

The gegenion associated with the active center oxonium ion must have a great effect on the course of redistribution and must determine to a large extent its importance.

Then, *Dreyfus et al.*[20] and *Yamada et al.*[21] have shown that simple anions like $Cl^-$ are not able to stabilize oxonium ions, and consequently the phosphazene oxonium ion complex must be very unstable with respect to the silylated derivative of (I) and $Me_3SiCl$ leading to a termination reaction.



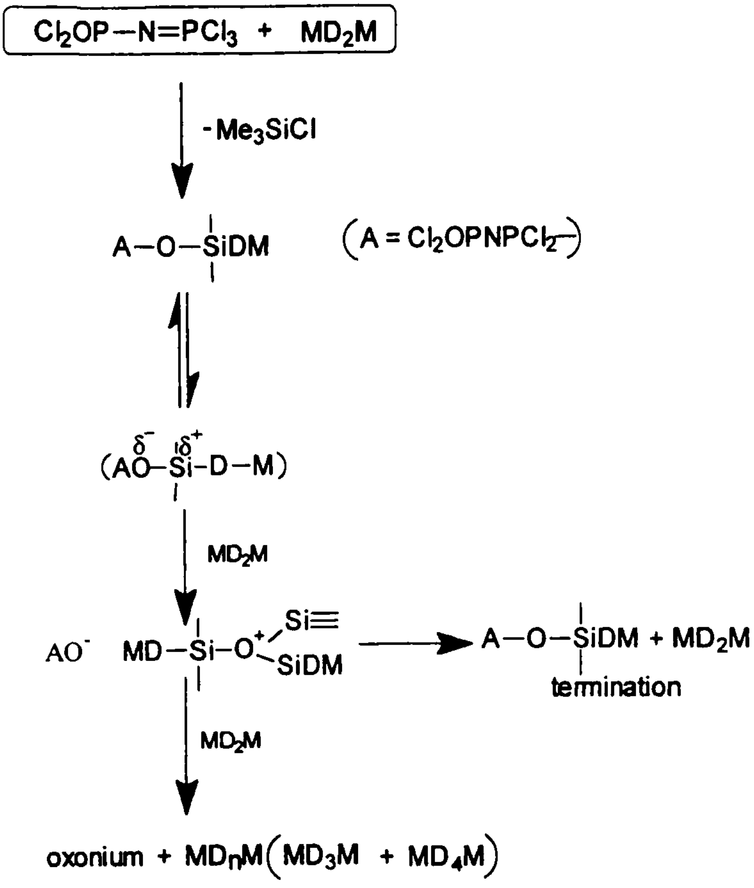
SCHEME 1

In any case, according to this mechanism, the redistribution should be low leading to silylated derivatives (III) with short-chain linear siloxane units attached to the phosphorus atom of (I). More, these last should be inactive for the redistribution process.

To check that, the study of the possible catalytic effect of these silylated phosphazenes has been made. It was shown, by gas chromatographic analysis that the addition of these compounds (synthesized from the reaction between (I) and $MD_2M$) to an excess of $MD_2M$ induced the redistribution reaction.

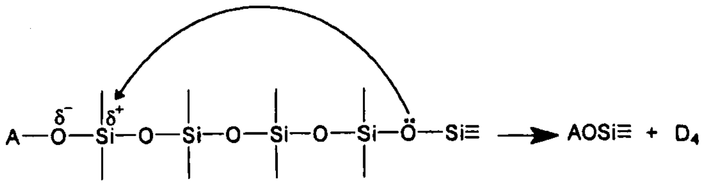
Therefore, this observation indicated that these silylated species were important reactive intermediates in this reaction, and it can be admitted that the siloxane oxonium ion can also result of the attack of a siloxane oxygen atom on the $Si^{\delta+}$ of (III), as represented in the scheme 2 in the case of $MD_2M$, the associated gegenion being in this case $Cl_2OPNPCl_2O^-$.

Whatever the active center origin may be, the formation of cyclic oligomers can be explained by intramolecular reactions concerning the

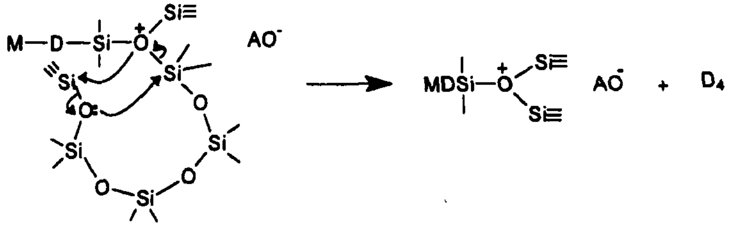


SCHEME 2

silylated derivatives (III) or the siloxane oxonium ion according to reactions (14) and (15) respectively.



(14)

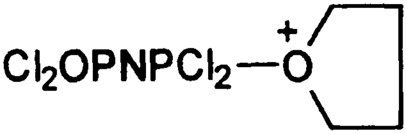


(15)

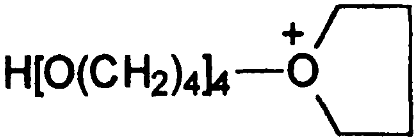
All these results can be compared to those we obtained with the studies of the reactions of (I) and (V) with tetrahydrofuran[22,23] which lead in the two cases to polytetrahydrofuran when a large excess of THF was used.

With a smaller molecular ratio THF/(I) or (V) (3 and 1), results were the formation of polytetrahydrofuran with short chains associated to $(Cl_2OP)_2N(CH_2)_4Cl$ with (I) and to $(Cl_2OP)_2N[(CH_2)_4\text{-}O]_n\text{-}H$ with (V).

In the two cases, the mechanism was based on the initial formation of the oxonium ions (VI) and (VII), followed by nucleophilic attack on carbon α of oxonium ions coming from the free electronic doublet on oxygen of THF.

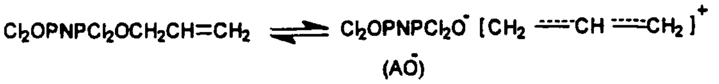


(VI)



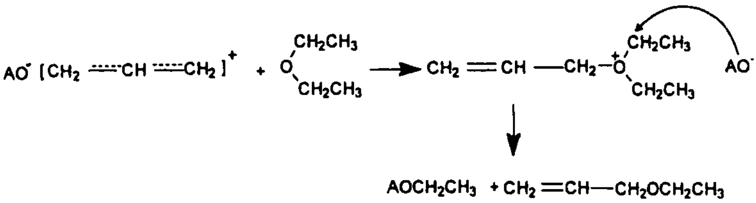
(VII)

These results are also in accordance with those obtained from the reaction between (I) and allyloxytrimethylsilane $Me_3SiOCH_2CH{=}CH_2$ leading at low temperature in diethylether to the oxygen derivative $Cl_2OP\text{-}N{=}PCl_2(OCH_2CH{=}CH_2)$ which reacts with the solvent to give the allylether and the ethoxyderivative $Cl_2OP\text{-}N{=}PCl_2(OCH_2CH_3)$[24]. The corresponding mechanism also involves the formation of an allylic cation according to the reactions (16) and (17).



$$Cl_2OPNPCl_2OCH_2CH{=}CH_2 \rightleftharpoons \underset{(AO^-)}{Cl_2OPNPCl_2O^-}\,[CH_2 \cdots CH \cdots CH_2]^+$$

(16)



(17)

## EXPERIMENTAL

The method described by *Seglin et al.*[25] was used to obtain (I).

It was purified by distillation under reduced pressure: bp 90°C (0.1 torr), yield 94%. Its purity was checked by elemental analysis (Cl, N, P) and $^{31}P$ NMR.

Anal.. $Cl_5NOP_2$:

Calc.: Cl, 65.86 N, 5.19; P, 23.0.

Found :Cl, 66.52; N, 5.19; P, 23.89.

$^{31}P$ NMR ($C_6H_6$): $\delta = +1.4$ ppm (d) ($N{=}PCl_3$); $\delta = -12.0$ ppm (d) ($N\text{-}P(O)Cl_2$); $^2J_{PNP} = 17$ Hz.

Toluene 99.8% and Acetonitrile (99.8%) were purchased from Aldrich and kept on a 4 Å molecular sieve.

Hexamethyldisiloxane (MM), decamethyltetrasiloxane ($MD_2M$) and dodecamethylpentasiloxane ($MD_3M$) were purchased from Aldrich. They were also kept on a 4 Å molecular sieve. Solvents and siloxanes were analysed by the Karl Fischer method before use (Hydromat 2 Prolabo France).

$^{31}P$ NMR spectra were made with a Bruker WP 300 spectrometer. The reference was 85% $H_3PO_4$.

$^{29}Si$ NMR spectra were made with a Bruker ASX 400 spectrometer. The reference was tetramethylsilane (TMS). For a quantitative analysis, a 45°

pulse width and inverse gate decoupling were used combined with a relaxation delay of 8 s when chromium III acethylacetonate [Cr(acac)$_3$] was used as relaxation reagent or with a relaxation delay of 200 s without [Cr(acac)$_3$].

Gas chromatographic analyses were performed with a Shimadzu GC-14A instrument equipped with a Schimadzu CR4A intergator. The chromatograph was fitted with a flame ionization detector, a column CPSiL 5CB (l=30m, d=0.53mm), temperature program [60 °C (10°C/mn) – 125 °C (5°C/mn) 150 °C (10°C/mn) – 230 °C], detector and injector temperatures 250°C. Dodecane was used as internal standard.

## Procedure

The glassware was washed, carefully dried and kept under nitrogen pressure. All operations were carried out under nitrogen atmosphere. Siloxanes were added to (I) and if necessary solvent in a three necked flask previously brought to the reaction temperature, and equipped with a dropping funnel, dry nitrogen inlet tube and $P_2O_5$ moisture guard columns. The mixture was magnetically stirred.

The evolution of the reaction was followed by $^{31}$P NMR analysis of samples taken at different times.

For the kinetic measurements, the reactions were performed within the NMR tubes. On grounds of solubility, the reactions of (I) with hexamethyldisiloxane (MM) were performed with toluene as solvent (molar ratios MM /(I)/ toluene = 1/1/1). With $MD_nM$ ($n = 2, 3$), the reactions were carried out in bulk. In these cases, a glove box was used to prepare a stock solution of (I) and siloxanes and for their introduction in a series of tubes which were then maintained in a thermostated bath at the required temperature. Each tube was then removed from the bath at a given time and analysed by $^{31}$P or $^{29}$Si NMR spectroscopy.

### *Acknowledgements*

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