Macromolecules **1985,** *18,* 139–144

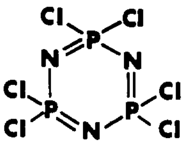
Reactions between Hexachlorocyclotriphosphazene and Hexamethylcyclotrisiloxane: Polymerization, Ring Cleavage, and Cross-Linking

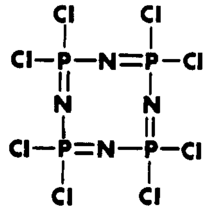
Harry R. Allcock,* David J. Brennan, and Robert W. Allen[1]

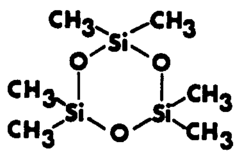
Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. Received August 8, 1984

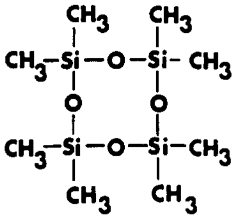
ABSTRACT: The reactions between (NPCl$_2$)$_3$ and (OSiMe$_2$)$_3$ at 250 °C have been investigated. Three main processes occur: siloxane ring–ring equilibration, homopolymerization of (NPCl$_2$)$_3$ to high polymeric (NPCl$_2$)$_n$, and siloxane skeletal cleavage by P–Cl bonds to yield cyclic phosphazenes bearing one or two ω-chlorosiloxane side groups. The formation of phosphazene polymers cross-linked by P–O–P bonds also occurs at later stages of the reaction. α,ω-Dichlorosiloxanes are liberated in this latter process. Similar reactions are evident when (NPCl$_2$)$_3$ reacts with (OSiMe$_2$)$_4$ or (Me$_3$Si)$_2$O. The interconnected reaction pathways that lead to these products are discussed.

Chlorocyclophosphazenes, such as (NPCl$_2$)$_3$ (1) or (NPCl$_2$)$_4$ (2), undergo a thermally induced ring-opening polymerization at temperatures above 210 °C.[2-7] It is also well-known that methylcyclosiloxanes, such as (OSiMe$_2$)$_3$ (3) or (OSiMe$_2$)$_4$ (4), oligomerize and polymerize at elevated temperatures, especially under the influence of basic or acidic catalysts.[8,9]


1


2


3

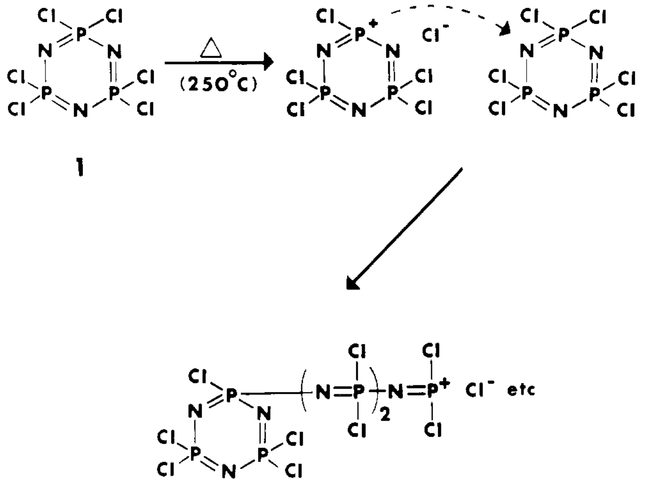

4

The mechanism of polymerization of chlorophosphazenes is believed to involve an initial ionization of a P–Cl bond and a cationic attack by the resultant phosphazenium ion on another trimer molecule (Scheme I).[4,7] The acid-catalyzed polymerization of (OSiMe$_2$)$_{3\mathrm{or}4}$ involves an initial skeletal cleavage by an acid, followed by a cationic attack by the resultant siliconium ion on another cyclosiloxane molecule (Scheme II).[10]

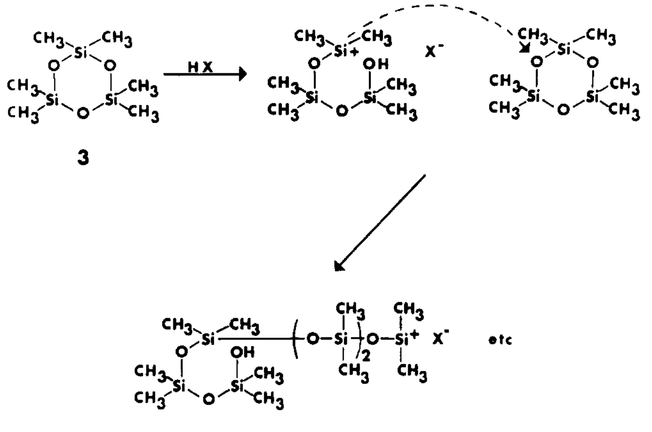
The similarity between these two mechanisms prompted us to investigate the reactions of chlorocyclophosphazenes with methylcyclosiloxanes under conditions that might be expected to lead to polymerization of the two participating species.

Initially, we wished to answer the following questions: (1) Do chlorocyclophosphazenes and methylcyclosiloxanes react in the molten state at elevated temperatures? (2) If so, does the interaction lead to a copolymerization or cooligomerization to generate hybrid siloxane–phosphazene species? (3) Can the chlorophosphazene function as a catalyst or initiator for the polymerization of the siloxane, and vice versa? (4) Can either reagent function as a skeletal cleavage-, chain transfer-, or chain-termination agent for the other? (5) If no reaction occurs, do either of the two species polymerize independently in a solvent system provided by the other?

Scheme I



Scheme II

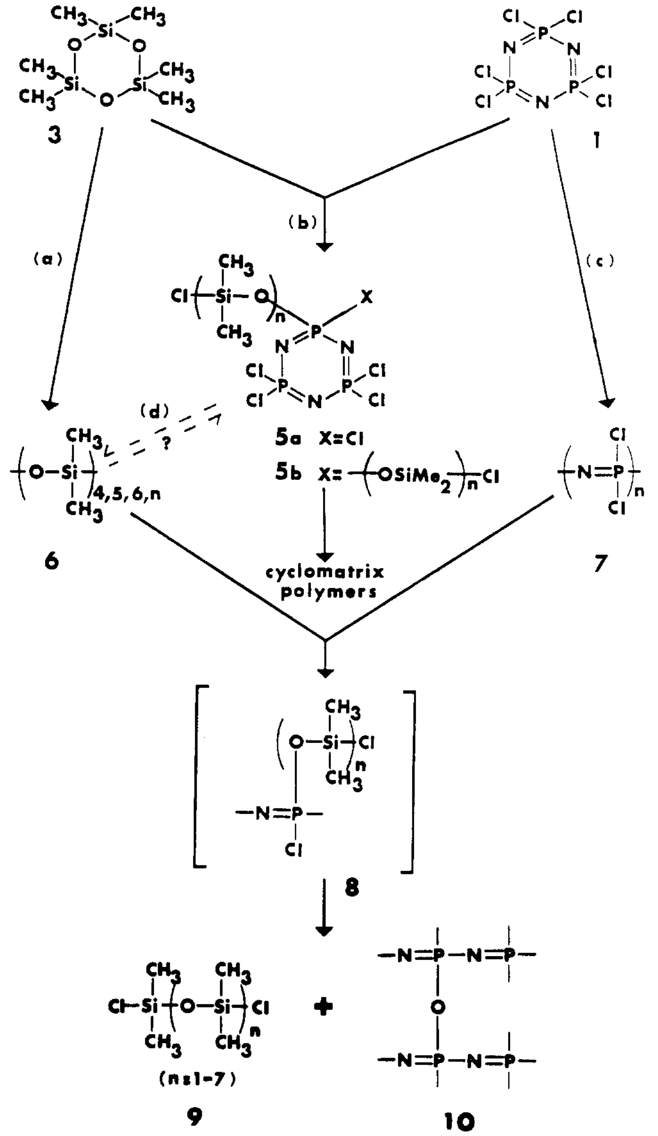


As will be shown, the interactions proved to be complex, with several of these possible reactions taking place simultaneously or sequentially.

The reactions studied in greatest detail were those between the two cyclic trimers (NPCl$_2$)$_3$ and (OSiMe$_2$)$_3$ at 250 °C. Although the cyclotetrasiloxane, 4, is the normal starting point for siloxane polymerizations, the cyclic trimer, (OSiMe$_2$)$_3$, is more reactive than the tetramer in ring–ring equilibration and polymerization reactions.[11] Thus, the reactions between the two trimers, (NPCl$_2$)$_3$ and (OSiMe$_2$)$_3$, appeared to provide a better match in reactivities than between (NPCl$_2$)$_3$ and (OSiMe$_2$)$_4$. However, some reactions between (NPCl$_2$)$_3$ and (OSiMe$_2$)$_4$ were also investigated.

0024-9297/85/2218-0139$01.50/0 © 1985 American Chemical Society

Scheme III



Results and Discussion

Overall Reaction Pattern. The results can be understood in terms of three main, concurrent reaction manifolds, as illustrated in Scheme III. These pathways are interconnected.

Pathway (a) involves the cyclooligomerization or polymerization of $(OSiMe_2)_3$ mainly to $(OSiMe_2)_{4-6}$, a reaction that is apparently assisted by $(NPCl_2)_3$. These siloxane products undergo eventual ring cleavage by $(NPCl_2)_3$ to yield cyclotriphosphazenes with ω-chlorosiloxane side groups or cleavage by $(NPCl_2)_n$ to generate P–O–P cross-linked phosphazene polymers and α,ω-dichlorosiloxanes.

Pathway (b) is the simplest prototype reaction between $(OSiMe_2)_3$ and $(NPCl_2)_3$. It results in siloxane skeletal cleavage by a P–Cl bond of the phosphazene to give two cyclophosphazene species with linear ω-chlorosiloxane side groups (**5a** and **5b**). This type of reaction may constitute an intermediate step (d) in the ring–ring equilibrations mentioned for pathway (a). A further extension of pathway (b) could lead to extensive cross-linking of cyclotriphosphazene rings by siloxane residues as cyclomatrix polymers and α,ω-dichlorosiloxanes are formed.

Pathway (c) involves the homopolymerization of $(NPCl_2)_3$ to linear, high polymeric $(NPCl_2)_n$ (**7**) in a solvent system that consists of $(OSiMe_2)_3$ and higher siloxane oligomers. The P–Cl bonds in the $(NPCl_2)_n$ high polymer eventually react with $(OSiMe_2)_{3...n}$ (generated via pathway (a)) to cleave the siloxane rings and form transient polyphosphazenes with pendent ω-chlorosiloxane side groups (**8**). Such species can eliminate α,ω-dichlorosiloxanes and yield cross-linked polyphosphazenes in which the linear chains are connected by P–O–P bonds. Pathway (c) is slower than the initial steps of pathways (a) and (b). Detectable amounts of $(NPCl_2)_n$ (**7**) are formed only after appreciable siloxane equilibration to **6** and some generation of **5** have occurred.

The primary evidence on which these pathways are based is the identification of species **5**, **6**, **7**, **9**, and **10**. This is discussed in more detail in the following sections.

Pathway (a). The conversion of $(OSiMe_2)_3$ to $(OSiMe_2)_{4-6}$ takes place after the first 5 h of reaction at 250 °C. For example, when a 3:2 molar ratio of $(NPCl_2)_3$ to $(OSiMe_2)_3$ was heated for a 20-h period, over 80% of the original amount of $(OSiMe_2)_3$ was converted to $(OSiMe_2)_{4-6}$, while 15% remained unreacted. Less than 5% was converted to **5** and virtually none was converted to **8**, **9**, or **10**. By comparison, when $(OSiMe_2)_3$ was heated in the absence of $(NPCl_2)_3$ at 250 °C for 408 h, only 55% was converted to higher analogues (30% $(OSiMe_2)_{4-6}$ and 25% $(OSiMe_2)_n$), while 45% remained unreacted. The cyclic oligosiloxanes were separated by vapor phase chromatography and were identified by mass spectrometry (see Experimental Section).

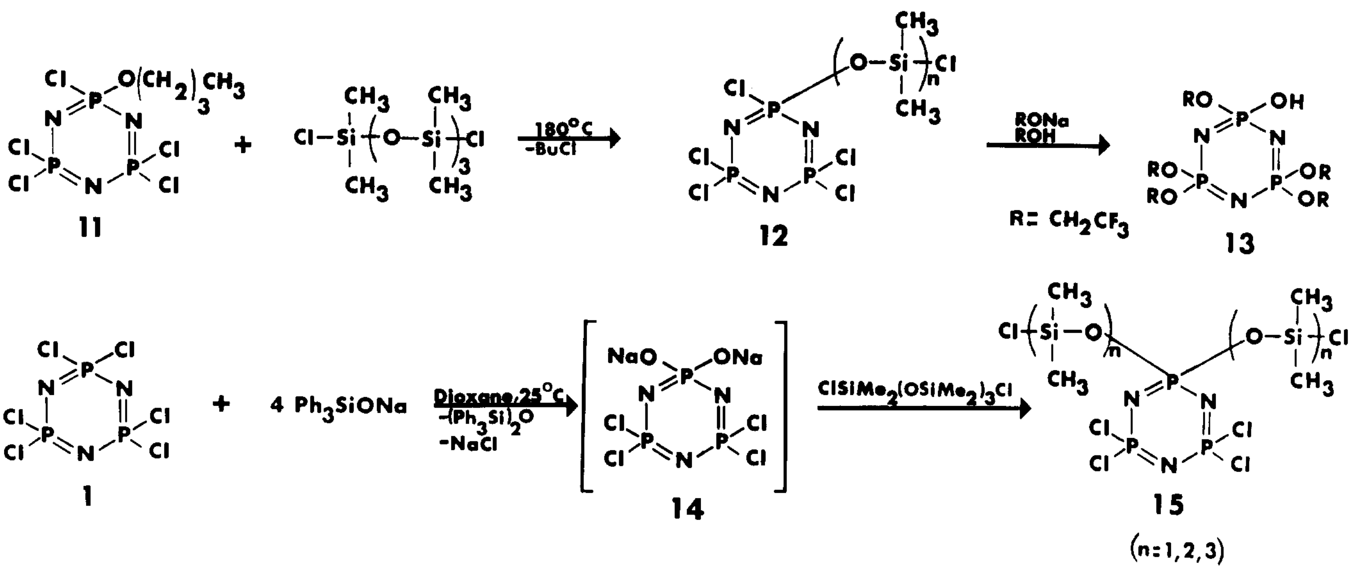
Beyond a certain point in the reaction, the amounts of cyclosiloxanes in the system decreased. The fate of these species is discussed in the following two sections.

Pathway (b). At an early stage in the reaction sequence, small quantities of oily products are formed that contain a cyclic phosphazene ring attached to a linear siloxane chain (**5a**) and a cyclic phosphazene ring substituted geminally by two linear siloxane chains (**5b**). The ^{31}P NMR spectrum of **5a** was an AB_2 spin pattern (A: 1.0 ppm, B: 22.0 ppm, J_{PNP} = 69.6 Hz) as was the ^{31}P NMR spectrum of **5b** (A: −18.5 ppm, B: 20.3 ppm, J_{PNP} = 80.1 Hz). These two low-yield products were nonvolatile and decomposed rapidly on contact with moisture due to the presence of the P–O–Si bonds.[13] It was thus necessary to confirm the structures of **5a** and **5b** through their synthesis via other routes.

Compound **5a** was identified by the preparation of the model compound **12**. It has been reported that monobutoxypentachlorocyclotriphosphazene (**11**) reacts with chlorodimethylphenylsilane to yield mono(dimethylphenylsiloxy)pentachlorocyclotriphosphazene along with the elimination of butyl chloride.[14] The analogous reaction of **11** with 1,7-dichlorooctamethyltetrasiloxane was carried out to yield the siloxypentachlorocyclotriphosphazene, **12** (Scheme IV). During the course of the reaction, the ^{31}P NMR AB_2 spin pattern associated with **11** (A: 15.2 ppm, B: 22.8 ppm, J_{PNP} = 60.2 Hz) disappeared and a new AB_2 pattern appeared for **12** that was identical with that of **5a**. Butyl chloride was eliminated during this process. The structure of hydrolytically unstable **12** was further confirmed by the preparation of the stable derivative, **13**, which was identified by ^{31}P NMR spectroscopy and mass spectrometry.

The identity of compound **5b** was confirmed by the preparation of the model compound **15** (Scheme IV). It is believed that the reaction of **1** with sodium triphenylsiloxide yields intermediate cyclotriphosphazene species that contain P–O–Na groups.[15,22] The reaction of **1** with 4 equiv of sodium triphenylsiloxide yielded a species believed to be **14**. Hexaphenyldisiloxane was also formed as

Scheme IV



a product during this reaction. Intermediate **14** was then allowed to react with 1,7-dichlorooctamethyltetrasiloxane to yield **15**. The ^{31}P NMR spectrum of **15** was identical with that of **5b**. Species **15** were identified by gas chromatography and mass spectrometry.

In a typical reaction between $(NPCl_2)_3$ and $(OSiMe_2)_3$ (1:1 ratio, at 250 °C for ~20 h), species **5** were detected in amounts that correspond to ~2% of the $(NPCl_2)_3$ initially present. The concentration of **5** then fell as the reaction proceeded. Thus, it seems likely that **5a** and **5b** are converted to other products in the later stages of the sequence. Heating of an isolated sample of **12** (model for **5a**) at 250 °C brought about its conversion to cyclosiloxanes (**6**), α,ω-dichlorosiloxanes (**9**), and cross-linked polymers. The cyclosiloxanes and α,ω-dichlorosiloxanes were separated and identified, as described previously.

Pathway (c). It was found that $(NPCl_2)_3$ polymerizes in the solvent system of siloxanes to yield the linear high polymer, $(NPCl_2)_n$ (**7**). At intermediate stages in the overall sequence (20–30 h at 250 °C) this polymer is the main phosphazene reaction product. Subsequently (>30 h), the $(NPCl_2)_n$ undergoes cross-linking to an insoluble material (**10**) with the concurrent liberation of α,ω-dichlorosiloxanes. The cross-links contain P–O–P linkages, as determined by infrared spectroscopy and microanalyses.

The evidence that $(NPCl_2)_3$ is converted initially to $(NPCl_2)_n$ is as follows. First, the viscosity of the reaction mixture rises as $(NPCl_2)_n$ is formed. The polyphosphazene can be isolated by the removal of the cyclosiloxanes and $(NPCl_2)_3$ under vacuum. A ^{31}P NMR spectrum of **7** in THF showed only a singlet at −18.9 ppm, the same value found for $(NPCl_2)_n$ prepared by the well-known melt polymerization of $(NPCl_2)_3$.[5,16] Polymer **7** was completely soluble in THF and toluene, and was, therefore, not cross-linked. An infrared spectrum of **7** matched that of an authentic sample of $(NPCl_2)_n$. Elemental analysis of **7** showed that less than 0.3% silicon was present, which would correspond to one $OSiMe_2$ group for every 85–90 $NPCl_2$ units. This indicates that **7** is formed initially as an entity separate from a species such as **8**. Polymer **7** was treated with sodium trifluoroethoxide to yield high polymeric $[NP(OCH_2CF_3)_2]_n$, a well-known and fully characterized compound.[5,17] This trifluoroethoxy derivative gave a singlet ^{31}P NMR spectrum at −7.3 ppm (lit.[5] −7.5 ppm).[16] The same derivative was found by GPC analysis to contain high polymeric fractions with molecular weights $>2 \times 10^6$ and 3×10^4. The trifluoroethoxy derivative of $(NPCl_2)_n$ prepared by conventional techniques[5] has a molecular weight of $>2 \times 10^6$.

The subsequent steps in this pathway involve the reaction of $(NPCl_2)_n$ with $(OSiMe_2)_{3...n}$ to yield an intermediate species **8**, and the subsequent crosslinking to **10** accompanied by α,ω-dichlorosiloxane liberation. The conversion of soluble **7** to the insoluble **10** takes place only in the later phases of the reaction. Furthermore, α,ω-dichlorosiloxanes are detected and isolated only during these later stages. The formation of **10** is also accompanied by a decrease in the concentration of cyclooligosiloxanes (**6**).

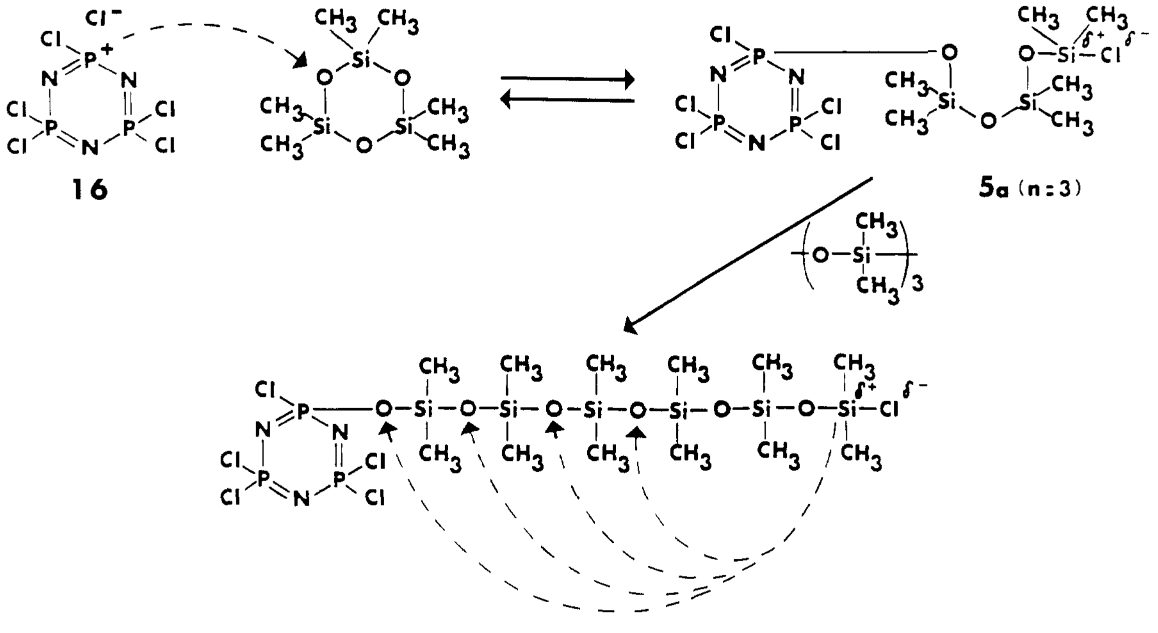
In a typical reaction, 88% of the $(NPCl_2)_3$ starting material is converted to **10** after 60 h at 250 °C, and >95% of the initial $(OSiMe_2)_3$ appears as α,ω-dichlorosiloxanes. The composition of **10** was deduced by microanalysis and by infrared spectroscopy. Elemental analysis of **10** indicated that, typically, 15% O and 29% P were present.[18] This corresponds to a polymer with approximately one oxygen atom for every phosphorus. The amount of silicon present (<2%) indicates that a few of the cross-links may contain siloxane units, but this value corresponds to only one silicon per 20 phosphorus atoms. Infrared spectroscopy provided further evidence for the structure of the crosslinked polymer, **10**. The infrared spectrum of **10** showed a P=N stretch at 1300–1200 cm^{-1} along with P–O–P absorptions at ~950 cm^{-1}. No evidence for the existence of C–H or Si–O bonds was found in the infrared spectrum of **10**.

The α,ω-dichlorosiloxanes were identified by gas chromatography/mass spectrometry, and by GC retention time comparisons with authentic samples. The range of products included those with from 2 to 8 silicon atoms in the chain.

The mechanism for the formation of **10**, as shown in Scheme III, is clearly an oversimplification in view of the multiplicity of siloxane species present and the presence of **5**. Both **5** and **8** could eliminate α,ω-dichlorosiloxanes as cross-linked matrices are formed. The fact that α,ω-dichlorosiloxanes appear to be formed only when insoluble cross-linked polymers are being generated is a key item of evidence for the mechanism. However, it was still necessary to demonstrate that **7** could react with **3** or **6** to form **9** and **10**.

A pure sample of $(NPCl_2)_n$, prepared by the conventional melt polymerization of $(NPCl_2)_3$,[5] was heated with

Scheme V



$(OSiMe_2)_3$ at 250 °C. The product mixture included the cross-linked high polymer, α,ω-dichlorosiloxanes, and the cyclosiloxanes, $(OSiMe_2)_{4-6}$. The ability of **12** to generate cyclomatrix polymers was confirmed, as mentioned earlier, by the conversion of **12** to **6**, α,ω-dichlorosiloxanes (**9**), and cyclomatrix polymers. Moreover, high molecular weight poly(dimethylsiloxane), prepared independently was found to react with $(NPCl_2)_3$ at 250 °C to yield small amounts of α,ω-dichlorosiloxanes, cross-linked phosphazene polymers, cyclosiloxanes (**6**), and low molecular weight $(OSiMe_2)_n$. By contrast, high polymeric $(OSiMe_2)_n$ did not depolymerize to cyclic oligomers when heated alone at 250 °C for the same time, but it did depolymerize in the presence of $(NPCl_2)_3$.

Thus, a key feature of these reactions is the ability of P–Cl bonds to cleave the Si–O skeletal bonds of cyclosiloxanes, polysiloxanes, and short-chain linear siloxane units attached to phosphazene rings or chains. Because attack by the P–Cl units can presumably take place at any site along a siloxane chain or around a ring, a complex mixture of products is generated as the reaction proceeds.

Reaction of $(NPCl_2)_3$ with $(OSiMe_2)_4$ or $(MeSi)_2O$. Similar considerations govern the reactions of $(NPCl_2)_3$ with octamethylcyclotetrasiloxane (**4**) or hexamethyldisiloxane. The reaction between $(NPCl_2)_3$ and $(OSiMe_2)_4$ at 250 °C initially yields an un-cross-linked, linear chlorophosphazene polymer (**7**). This was converted to $[NP(OCH_2CF_3)_2]_n$ by treatment with sodium trifluoroethoxide, and the derivatized polymers were identified by ^{31}P NMR methods. Subsequent reaction brought about cross-linking of the polymer and liberation of the α,ω-dichlorosiloxanes.

The reaction between $(NPCl_2)_3$ and $(Me_3Si)_2O$ at 250 °C similarly involved an initial solution polymerization of $(NPCl_2)_3$ to linear $(NPCl_2)_n$, followed by cross-linking as Me_3SiCl was liberated.

The Siloxane Equilibration Mechanism. It is known that $(Me_3Si)_2O$ undergoes Si–O bond cleavage with $POCl_3$[19] or PCl_3[20] to give Me_3SiCl and that $(OSiMe_2)_4$ is cleaved by PCl_5 to yield Me_2SiCl_2.[21] The cleavage of Si–O bonds by the P–Cl units in $(NPCl_2)_3$ or $(NPCl_2)_n$ appears to follow that same pattern.

The mechanisms of polymerization of $(NPCl_2)_3$ is believed to involve the heterolytic cleavage of a P–Cl bond.[7] It seems reasonable to suppose that electrophilic attack by the resultant phosphazenium ion (**16**) on an oxygen atom of the siloxane would lead to Si–O bond cleavage to yield a species such as **5a** (n = 3) (Scheme V).

The terminal Si–Cl bond could then induce Si–O bond cleavage in another $(OSiMe_2)_3$ molecule (chain growth) or bite back on its own chain to generate a range of different cyclosiloxanes. Such a mechanism could account for both the presence (in low concentrations) of **5** and the siloxane ring–ring equilibration process. In this sense, the $(NPCl_2)_3$ functions as a catalyst for siloxane ring–ring equilibration. (However, so far, we have been unable to demonstrate that at much lower concentrations it behaves as a catalyst for cyclosiloxane polymerization.)

The same type of mechanism probably operates when $(NPCl_2)_n$ reacts with $(OSiMe_2)_{3-6}$ to generate intermediate **8** and the cross-linked polymers **10**.

Experimental Section

Materials. Hexachlorocyclotriphosphazene (**1**) was kindly provided by the Firestone Tire and Rubber Co. It was sublimed before use to remove small amounts of octachlorocyclotetraphosphazene (**2**). Hexamethylcyclotrisiloxane (**3**), octamethylcyclotetrasiloxane (**4**), 1,3-dichlorotetramethyldisiloxane, 1,5-dichlorohexamethyltrisiloxane, and 1,7-dichlorooctamethyltetrasiloxane were obtained from Petrarch Systems, Inc. and were used as received. Trifluoroethanol (Halocarbon Products) was dried over molecular sieves before use. Poly(dimethylsiloxane) (Cellomer Associates) was used as received. Tetrahydrofuran (THF), 1,4-dioxane, and hexane were dried over sodium benzophenone ketyl and were distilled before use. Thick-walled Pyrex tubes (19 mm o.d.) constricted at a length of 15 cm (sealed volume of approximately 20 mL) were used for all reactions.

Analytical Techniques. ^{31}P NMR (^1H decoupled) spectra were obtained with JEOL PS-100 FT NMR and Varian CFT-20 NMR spectrometers. ^{31}P NMR chemical shifts are relative to 85% H_3PO_4 with positive shift values downfield from the reference. Gas chromatographic analysis was carried out with a Varian 3700 gas chromatograph with a 6-ft OV-101 packed glass column. GC–MS analysis made use of a Finnegan 3200 mass spectrometer with a Finnegan 6000 data system and a Finnegan 9500 gas chromatograph. A 25-ft OV-101 capillary column was used. Gel permeation chromatography was performed with the use of a Waters Associates ALC/GPC 501 instrument with 500-, 10^3-, 10^4-, 10^5-, and 10^6-Å μ-Styragel columns. Infrared spectra were obtained by using a Perkin-Elmer 283B grating spectrometer. Elemental analyses were obtained by Galbraith Laboratories.

Polymerization of $(OSiMe_2)_3$ at 250 °C. A clean Pyrex tube was dried in a 130 °C oven for 24 h. Hexamethylcyclotrisiloxane (8.0 g, 0.036 mol) was introduced into the tube. The tube was evacuated for 30 s to remove most of the air. The dynamic vacuum was interrupted, and the tube was immersed in a liquid nitrogen bath at −196 °C for 2 min. Evacuation of the tube was then continued at 0.02 mmHg for 15 min at −196 °C. The tube was then sealed, wrapped in a wire mesh screen, and heated in a thermoregulated oven (fitted with a mechanical tube rocker) at 250 °C for 408 h. After this time, the contents of the tube became viscous. The tube was cooled to room temperature before being opened. The contents were transferred to a small vacuum sublimator and were heated at 80 °C for 24 h. The volatile materials were collected in a trap cooled to −196 °C and were identified as $(OSiMe_2)_{3-6}$ by a combination of gas chromatography and mass spectrometry (GC–MS) along with GC retention time comparisons with known samples ($n = 3$ and 4). The cyclosiloxanes $(OSiMe_2)_{4-6}$ comprised 40% of the total cyclic species (30% overall yield) while the $(OSiMe_2)_3$ accounted for 60% of the cyclic species present (45% overall recovery). Poly(dimethylsiloxane) was obtained as a nonvolatile residue and was identified by infrared spectral comparison with an authentic sample (yield 2.0 g, 25%).

Formation of $(OSiMe_2)_{4-6}$ during the Reaction between $(NPCl_2)_3$ and $(OSiMe_2)_3$ at 250 °C. In a typical experiment, a 1:1 molar ratio of reactants was used [$(NPCl_2)_3$ (9.38 g, 0.0270 mol) and $(OSiMe_2)_3$ (6.00 g, 0.0270 mol)]. The sealed tubes were heated for less than 30–40 h to form the mixture of cyclosiloxanes as the only volatile siloxane products. The volatile cyclosiloxanes were collected by opening the tubes in a nitrogen-filled glovebag, transfer of the contents of each tube into a vacuum sublimator, and removal of the volatile contents at 80 °C for 10–12 h. The volatile cyclosiloxanes were collected in a trap cooled to −196 °C and were identified by GC retention time comparison with known samples and by GC–MS. Unreacted $(NPCl_2)_3$ and traces of $(NPCl_2)_4$ were collected on a cold finger at 10 °C and were identified by ^{31}P NMR spectroscopy (singlets at +21.4 and −5.8 ppm, respectively). Generally, more than 70% of the $(NPCl_2)_3$ was recovered.

Formation of $ClSiMe_2(OSiMe_2)_{1-7}Cl$ and Cross-Linked Polymers. In a typical experiment $(NPCl_2)_3$ (7.00 g, 0.0202 mol) and $(OSiMe_2)_3$ (4.50 g, 0.0202 mol) were used. The tube was heated at 250 °C until a white, immobile, elastomeric polymer formed in the tube (~40 h) along with a clear, nonviscous liquid. Continued heating at this stage brought about the formation of a hard, brittle, cross-linked polymer. The tube was then cooled to room temperature, was opened in a nitrogen filled glovebag, and the contents were transferred to a vacuum sublimator. The products were heated at 80 °C for 12 h, and the linear α,ω-dichlorosiloxanes were collected in a trap at −196 °C. The products were identified by GC retention time comparison with authentic samples and by GC–MS. Species $ClSiMe_2(OSiMe_2)_{2,3}Cl$ were generally formed in the largest quantities. The cyclic siloxanes $(OSiMe_2)_{4-6}$ were also shown to be present by the use of the same analytical techniques, but the concentrations of these species relative to α,ω-dichlorosiloxanes decreased as the reaction time and the degree of polymer cross-linking increased. The amount of $(NPCl_2)_3$ recovered decreased as the amount of cross-linked polymer increased. The cross-linked polymers were purified for microanalysis by removal of most of the siloxane and phosphazene species under vacuum. The polymer was then Soxhlet-extracted with dry hexane and dry toluene (7 days each) in an atmosphere of dry nitrogen. Residual solvent was removed under vacuum for 7 days.

Reaction of $(NPCl_2)_n$ with $(OSiMe_2)_3$ at 250 °C. Poly(dichlorophosphazene) (7.00 g, 0.0603 unit mol), prepared by the bulk polymerization of $(NPCl_2)_3$ in the absence of siloxanes, was heated with $(OSiMe_2)_3$ (4.50 g, 0.0202 mol) in a sealed Pyrex tube at 250 °C for 36 h. When cooled, the contents of the tube consisted of $(NPCl_2)_n$ and a clear, nonviscous liquid. The contents of the tube were heated in a vacuum sublimator at 80 °C for 24 h. The volatile products were collected in a trap at −196 °C and were identified by gas chromatography as $(OSiMe_2)_{4-6}$ and $ClSiMe_2[OSiMe_2]_{1-7}Cl$. The ring-cleaved α,ω-dichlorosiloxane species were present as 25% of the volatile products, while the cyclosiloxanes constituted 75% of the non-polymeric components. The polymer was no longer soluble in THF but swelled in this solvent in the manner expected for a lightly cross-linked macromolecule.

Reaction of $(NPCl_2)_3$ with $(OSiMe_2)_n$ at 250 °C. Hexachlorocyclotriphazene (5.40 g, 0.0156 mol) and poly(dimethylsiloxane) (4.70 g, 0.0634 unit mol) were heated at 250 °C for 36 h in an evacuated, sealed Pyrex tube. During the heating period the contents of the tube became noticeably less viscous and a white, immobile solid formed. The tube was cooled to room temperature and was opened in a nitrogen-filled glovebag. The contents of the tube were heated at 80 °C for a period of 24 h in a vacuum sublimator. The volatile species, collected in a trap at −196 °C, were identified by gas chromatography as $(OSiMe_2)_{4-6}$ and $ClSiMe_2(OSiMe_2)_{1-7}Cl$ in a 9:1 ratio. Species $(NPCl_2)_3$ was collected on a cold finger at 10 °C and was recovered in an 85% yield (identified by a ^{31}P NMR singlet at 21.4 ppm). The nonvolatile reaction products consisted of cross-linked phosphazene high polymer and low molecular weight poly(dimethylsiloxane).

Control Reaction: Effect of Heating $(OSiMe_2)_n$ at 250 °C. Poly(dimethylsiloxane) (4.70 g, 0.0634 unit mol) was heated at 250 °C for 36 h in an evacuated Pyrex tube. The polymer retained its bulk viscosity during this treatment. The tube was then cooled to 25 °C and opened, and the contents were heated at 80 °C in a vacuum sublimator for 24 h. No volatile species were collected in the trap at −196 °C, nor were any volatile products collected on the cold finger at 10 °C. Solution viscosity measurements of the poly(dimethylsiloxane) sample before and after heating at 250 °C showed no changes in molecular weight. Thus, the poly(dimethylsiloxane) was apparently unaffected by the heating at 250 °C in the absence of $(NPCl_2)_3$.

Formation of $N_3P_3Cl_5(OSiMe_2)_nCl$ (5a) and *gem*-$N_3P_3Cl_4[(OSiMe_2)_nCl]_2$ (5b). $(NPCl_2)_3$ (7.00 g, 0.0202 mol) and $(OSiMe_2)_3$ (4.50 g, 0.0202 mol) were heated together at 250 °C for 5–20 h. Under these conditions, no $(NPCl_2)_n$ or cross-linked polymers were formed. The tube was cooled to room temperature and opened in a nitrogen-filled glovebag. The contents of the tube were placed in a vacuum sublimator and heated at 80 °C for 24 h to remove residual $(NPCl_2)_3$ and allow cyclosiloxane oligomers to distill from the mixture. The sublimation residue consisted of a clear viscous oil. The oil was found to contain linear siloxane units by infrared spectral comparison with poly(dimethylsiloxane). The presence of cyclotriphosphazenes **5a** and **5b** was confirmed by the preparation of model compounds **12** and **15**, respectively. The ^{31}P NMR spectrum of **12** was identical with the spectrum of **5a**, and the ^{31}P NMR spectrum of **15** was identical with that of **5b**. Compounds **5a** and **5b** were formed in approximately equal quantities. The total yield of species **5a** and **5b**, based on recovered $(NPCl_2)_3$, was 1–2%.

Synthesis of $N_3P_3Cl_5(OSiMe_2)_nCl$ (12): A Model Compound for 5a. Monobutoxypentachlorocyclotriphosphazene (**11**) was prepared in THF by the reaction between $(NPCl_2)_3$ and sodium *n*-butoxide using a known procedure.[14] A mixture of **11** (1.77 g, 0.00459 mol) and 1,7-dichlorooctamethyltetrasiloxane (3.20 g, 0.00910 mol) was sealed in an evacuated glass tube and heated at 180 °C for 60 h. The tube was then cooled to 25 °C and opened in a nitrogen-filled glovebag. ^{31}P NMR analysis of the contents of the tube showed that **11** had been completely converted to **12**. The contents of the tube were transferred to a distillation apparatus and were heated at 130 °C (0.05 mmHg). Butyl chloride, cyclosiloxanes, and α,ω-dichlorosiloxanes were collected as volatile species and were identified by gas chromatography/mass spectrometry. Compound **12** remained as residue and did not distill on further heating. Conversion of **12** to **13** was carried out in THF by the reaction of **12** with sodium trifluoroethoxide. The trifluoroethoxy derivative (**13**) showed a parent ion in the mass spectrum at 647 amu, which was consistent with the structure of **13**. The ^{31}P NMR spectrum of **13** was an AB_2 spin pattern (A: 10.0 ppm, B: 19.0 ppm, $J_{PNP} = 73.0$ Hz), which matched the literature values.[15]

Synthesis of *gem*-$N_3P_3Cl_4[(OSiMe_2)_nCl]_2$ (15) ($n = 1, 2, 3$): A Model for Compound 5b. Triphenylsilanol (15.9 g, 0.0576 mol) was dissolved in dry dioxane (100 mL) and was added cautiously to a suspension of NaH (1.38 g, 0.0576 mol) in dry dioxane (100 mL) under an atmosphere of dry nitrogen. The reaction mixture was then stirred for 3 h. The sodium triphenylsiloxide solution was then added dropwise to a solution of $(NPCl_2)_3$ (5.00 g, 0.0144 mol) dissolved in dry dioxane (100 mL). The reaction mixture was then stirred for 6 h. A portion of this solution was evaporated to dryness, washed successively with hexane and water, and then recrystallized from hexane. The white solid remaining was identified as $Ph_3SiOSiPh_3$ by melting point

(224–226 °C) and by infrared spectral comparison with an authentic sample. To the reaction mixture was then added 1,7-dichlorooctamethyltetrasiloxane (10.5 g, 0.030 mol) and the reaction mixture was stirred for 3 h. ^{31}P NMR analysis showed that **15** had formed and had a spectrum identical with that of **5b**. The reaction mixture was filtered under nitrogen, the dioxane was removed under reduced pressure, and dry hexane was added. The resultant solution was then cooled to 0 °C and was filtered under nitrogen to remove $Ph_3SiOSiPh_3$. The filtrate was evaporated to dryness under reduced pressure and the residue was vacuum distilled (160–180 °C/0.05 mmHg) to yield species **15**, identified by gas chromatography/mass spectrometry techniques.

Formation of $(NPCl_2)_n$ from $(NPCl_2)_3$ in $(OSiMe_2)_3$. In a typical experiment $(NPCl_2)_3$ (7.00 g, 0.0202 mol) and $(OSiMe_2)_3$ (4.50 g, 0.0202 mol) were heated together at 250 °C until the solution became slightly viscous ($\simeq$24 h) but remained clear. The tube was cooled to room temperature and was opened in a nitrogen-filled glovebag. The contents were transferred to a vacuum sublimator and heated at 80 °C until all the volatile species had been removed. The white polymeric residue was identified as $(NPCl_2)_n$ by ^{31}P NMR spectroscopy (singlet at −18.8 ppm). The polymer was purified for elemental analysis by precipitation 3 times from dry THF into dry hexane in a nitrogen-filled glovebag. The yield of the unpurified polymer was typically 1.8 g (26%), based on the amount of $(NPCl_2)_3$ recovered.

Reactions of $(NPCl_2)_3$ with $(OSiMe_2)_4$ or $(Me_3Si)_2O$. The reaction times at 250 °C ranged from 21 to 158 h, with ratios of $(NPCl_2)_3$ to $(OSiMe_2)_4$ being varied from 1.5:1 to 36:1, and of $(NPCl_2)_3$ to $(Me_3Si)_2O$ from 1:1 to 10:1.

Acknowledgment. We thank the National Science Foundation Polymers Program and the U.S. Army Research Office for the support of this work. We also acknowledge the technical assistance provided by M. S. Connolly, J. L. Desorcie, and K. D. Lavin.

Registry No. 1, 940-71-6; 3, 541-05-9; 4, 556-67-2; $(Me_3Si)_2O$, 107-46-0.

References and Notes

(1) Deceased 1978. Some of the initial studies on which this paper is based appeared in the Ph.D. thesis by Robert W. Allen, submitted to The Pennsylvania State University in August 1976.
(2) Stokes, H. N. *Am. Chem. J.* **1897**, *19*, 782.
(3) Allcock, H. R. "Phosphorus-Nitrogen Compounds"; Academic Press: New York, 1972.
(4) Allcock, H. R. *Chem. Rev.* **1972**, *72*, 315.
(5) Allcock, H. R.; Kugel, R.L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709.
(6) Konecney, J. O.; Douglas, C. M. *J. Polym. Sci.* **1959**, *36*, 195.
(7) Allcock, H. R.; Best, R. J. *Can. J. Chem.* **1964**, *42*, 447.
(8) Hurd, D. T.; Osthoff, R. C.; Corrin, M. L. *J. Am. Chem. Soc.* **1954**, *76*, 249.
(9) Kantor, S. W.; Grubb, W. T.; Osthoff, R. C. *J. Am. Chem. Soc.* **1954**, *76*, 5190.
(10) Eaborn, C. "Organosilicon Compounds"; Butterworth: London, 1960; pp 259, 260.
(11) $(NPCl_2)_3$ polymerizes at 250 °C to give approximately a 40% yield of high polymeric $(NPCl_2)_n$ in ~8–24 h. In the absence of added initiators, hexamethylcyclotrisiloxane (**3**) was found to yield 25% high polymer and 30% $(OSiMe_2)_{4-6}$ after 17 days at 250 °C. The cyclic tetramer $(OSiMe_2)_4$ is virtually unreactive under the same conditions. By contrast, $(OSiMe_2)_4$ is converted to high polymer in 80% yield in 5 h at 160 °C[12] in the presence of ionic initiators, and $(OSiMe_2)_3$ polymerizes even faster.[9]
(12) Mansfield, R. A. *Macromol. Synth.* **1972**, *4*, 65.
(13) Borisov, S. N.; Voronkov, M. G.; Lukevits, E. Ya. "Organosilicon Derivatives of Phosphorus and Sulfur"; Plenum Press: New York–London, 1971.
(14) Belykh, S. I.; Zhivukhin, S. M.; Kireev, V. V.; Kolesnikov, G. S. *Russ. J. Inorg. Chem.* **1969**, *14* (5), 668.
(15) Allcock, H. R.; Fuller, T. J.; Matsumara, K. *Inorg. Chem.* **1982**, *21*, 515.
(16) The sign convention for ^{31}P NMR spectra has been changed since, for example, ref 3 and 5 were published.
(17) We recognize the possibility that treatment of $(NPCl_2)_n$ with sodium trifluoroethoxide could remove siloxane residues attached as side groups to the phosphazene chain. However, the elemental analyses of the polymer before derivatization provided evidence that the siloxane side groups (or end groups) existed in very low concentrations at this stage.
(18) A representative analysis showed the following: C, 1.94%; H, 1.04%; N, 13.73%; P, 29.10%; Si, 1.09%; Cl, 37.99%; and O, 15.10% (by difference).
(19) Schmidt, M.; Schmidbauer, H.; Binger, A. *Chem. Ber.* **1960**, *93*, 872.
(20) Voronkov, M. G.; Skorick, Yu. I. *Zh. Obshch. Khim.* **1965**, *35*, 106.
(21) Me_2SiCl_2 was detected after $(OSiMe_2)_4$ (2.9, 0.0097 mol) and PCl_5 (4.0 g, 0.019 mol) were heated in an evacuated sealed tube at 195 °C for 18 h.
(22) Allcock, H. R.; Fuller, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2250.

Thermodynamics of Polymerization for *cis*- and *trans*-Polyalkenamers and Its Application to the Polymerization of Cyclopentene

A. Drapeau and J. Leonard*

Groupe de Recherches sur les Macromolécules and Département de Chimie, Université Laval, Québec, G1K 7P4 Canada. *Received March 8, 1984*

ABSTRACT: *cis*- and *trans*-polyalkenamers may be obtained from equilibrium polymerizations of a certain number of monomers. The thermodynamics of these polymerizations is reexamined by taking into account the fact that the polymer is made of two types of distinguishable monomer units. A free energy term for the distribution of the cis and trans units in the polyalkenamer is added to the free energy for the conversion of pure monomer into pure amorphous *cis*- and *trans*-polyalkenamers. From the derived equation it is found that, for a given temperature, the proportion of cis and trans units in the polymer ought to be unique and independent of the solvent used when the configuration of the polyalkenamer is thermodynamically controlled. The equilibrium monomer concentration depends on the solvent and the configuration of the polymer formed. The equations are applied to the equilibrium polymerization of cyclopentene into polypentenamer at various temperatures with various catalysts. Computed values are in good agreement with reported experimental values.

Polymerization of dienes and cycloalkenes usually leads to the formation of linear unsaturated polymers (polyalkenamers) having one double bond per monomer unit. Depending on the catalysts used the configuration of the double bonds would be predominantly cis or trans. In the case of cycloalkenes, an equilibrium between monomer and active polymer can be reached in a certain number of polymerizations.[1-3] Since the free energy of polymerization