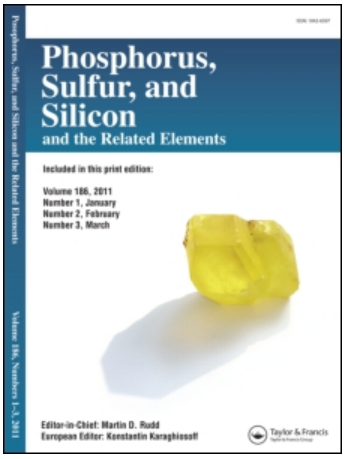

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REACTION PATHWAYS IN THE THERMOLYSIS OF (2-OXYETHYL-METHACRYL)PENTACHLOROCYCLOTRIPHOSPHAZENE

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Abstract The (2-oxyethyl methacryl) pentachlorocyclotriphosphazene, $N_3P_3Cl_5OCH_2CH_2OC(O)C(Me)=CH_2$ (1), has been shown to undergo a slow rearrangement to the corresponding phosphazane (2). Monitoring of the rate of rearrangement over temperature range of 35° to 111° shows a first order process in 1 with a positive enthalpy and negative entropy of activation. A mechanism based on tightly bound ion pairs and transfer of the $CH_2CH_2C(O)C(CH_3)=CH_2$ moiety to the nitrogen center is proposed. A hydrolysis product, $N_3P_3Cl_5OH$ and significant amounts of the unique oxo-bridged dimer, $N_3P_3Cl_5OP(O)NCH_2CH_2OC(O)C(Me)=CH_2(NPCl_2)_2$ (3) have also been observed. The identity of 3 was established by ^{31}P COSY experiments and mass spectrometry. The formation of these products can be related to the proposed mechanistic pathway. The rearrangement in related oxyalkylalkylphosphazenes has been explored.

INTRODUCTION

In the phosphazene/phosphazane rearrangement a N=P(OR)R′ unit undergoes tautomerization to the NRP(O)R′ moiety[1]. Although this transformation is of fundamental importance in limiting the stability of both cyclic and polymeric phosphazenes, a detailed understanding of the rearrangement is not available. Authenticated examples of uncatalyzed phosphazene/phosphazane rearrangements are limited to methoxyphosphazenes[1] such as persubtituted trimers and tetramers[2,3], geminal and non-geminal $N_3P_3R_2(OMe)_4$ (R=NMe_2, Ph)[4] and mixed alkoxy/arloxy derivatives e.g. $N_3P_3(OC_6H_4\text{-}p\text{-}Me)_3(OMe)_3$[5]. Product studies provide evidence for an intermolecular[2] and mixed inter- and intramolecular routes[5]. Kinetic studies[2,3] have been complicated by autocatalysis and the fact that several tantomerizations occur on going from reactant to product. In this paper, we report the first well characterized example of a phosphazene/phosphazane rearrangement involving a chlorophosphazene and a detailed mechanistic study of the process.

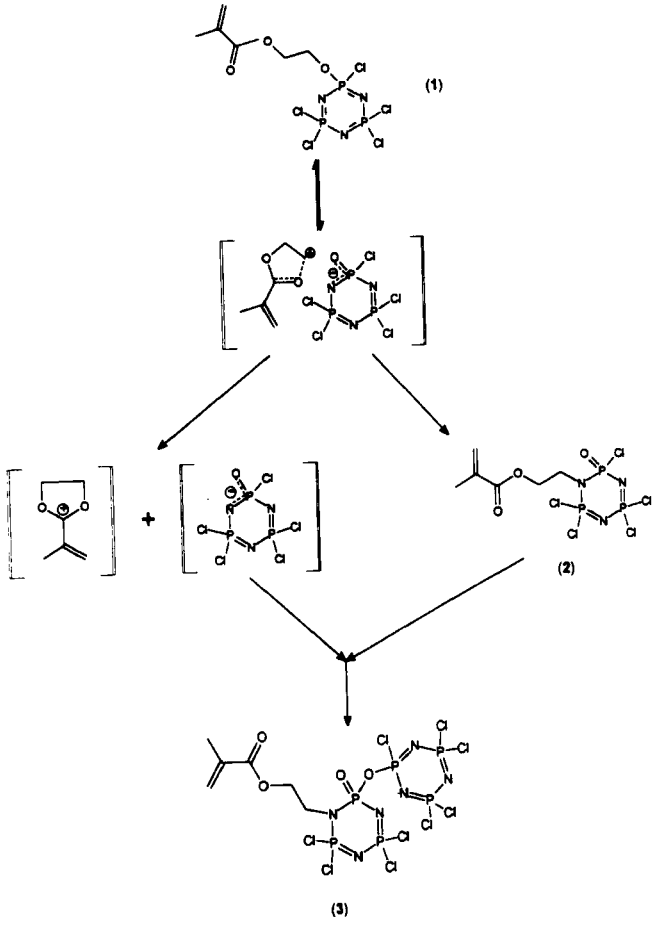
RESULTS AND DISCUSSION

The ^{31}P NMR spectrum of (2-oxyethyl methacryl)hexachlorocyclotriphosphazene (1) consists of a doublet at 23.6 ppm due to the PCl_2 centers and a triplet at 16.3 ppm

from to the PClOR phosphorus. After several weeks at room temperature (or several hours at higher temperatures), the resonances due to **1** decrease in intensity and several new signals appear. The new signals in the ^{31}P NMR spectrum were from the phosphazene-phosphazane rearrangement product, 2-(ethyl methacryl)-1-oxy-1,3,3,5,5-pentachlorocyclo-3,5-diphosphazene (**2**); the POCl center at -9.5 ppm, the PCl_2 center para to the phosphazane nitrogen at 17.7 ppm, and the PCl_2 center adjacent to the phosphazane nitrogen at 29.0 ppm. A COSY experiment confirmed the assignments made for **1** and **2** and revealed interesting connectivity which showed the presence of an oxo bridged dimer (**3**). The lowest frequency signal was at -20.0 ppm, a triplet of doublets, was attributed to a P(O)O center at one side of the oxo bridge. The next highest frequency signal was found at 6.8 ppm, a triplet of doublets ,was assigned to the POCl center on the other side of the oxo bridge. The resonance at 17.6 ppm, a doublet of doublets, is assigned to the PCl_2 center para to the phosphazane nitrogen. The signal at 23.4 is attributed to the PCl_2 units on the *tri*phosphazene ring. The highest frequency resonance, 30.0 ppm, was assigned to the PCl_2 center adjacent to the phosphazane nitrogen. The chemical shifts for the *di*phosphazene portion of **3** are similar to those of **2**, while the chemical shifts of the *tri*phosphazene portion of **3** are in agreement with those of an oxo bridged dimer reported by van de Grampel[6]. The mass spectrum clearly shows the presence of **3** at a molecular weight of 735 (M+1). In addition, ions corresponding to **3** after loss of the ester group and to **3** after loss the ester and an oxygen atom at 605. The isotope distributions for the ions were calculated and agree with the observed isotopic distributions. Signals characteristic of hydroxypentachlorocyclotriphosphazene (**4**), a hydrolysis product, previously observed by Haw[7], were evident in the ^{31}P NMR spectra from the rearrangement experiments. Experiments run on "dry" samples showed significantly less **4** present in the mixture and more **2** and **3**.

The rearrangement reaction was followed by ^{31}P NMR as a function of temperature. The loss in intensity of the resonance at 16.3 ppm (the PClOR center of **1**) over time was monitored at 111, 89, 70, 50, and 35°C in d_6-toluene and in all cases the reaction was allowed to proceed up to or beyond two half-lives. At all temperatures the rate was found to follow a first order rate law. Half-lives for the rearrangement ranged from 5.0 hours at 111°C to 81 days at 35°C. A mechanism for rearrangement has been proposed. The first and rate determining step is the dissociation of **1** into an solvent caged ion pair, a oxyphosphazene anion and a dioxolane stabilized carbocation which collapses into **2** when the oxyphosphazene nitrogen attacks the carbocation, if the oxyphosphazene oxygen attacks the

carbocation; **1** is regenerated. As the concentration of **2** rises during the reaction, it will trap oxyphosphazene that has diffused out of the solvent cage, generating **3**. The dissociation of **1** into a ion pair is consistent with the first order behavior. In addition, the proposal that the ions be in a tightly bound pair in a solvent cage, and that the carbocation is stabilized by the formation of a dioxolane ring, is consistent with the large negative $\Delta S^{\ddagger}$ value. In order to test the mechanism several other oxyalkyl methacryl phosphazenes were examined.



A spirocyclic alkoxyphosphazene, (2,3-dioxypropyl methacryl)tetrachlorocyclotri-phosphazene (**5**), was subjected to the harshest rearrangement conditions. The ^{31}P NMR spectrum showed no change during the course of the reaction and it was concluded that no rearrangement, hydrolysis, or

degradation occurred. In the separated monocation/monoanion pair from **5** the nitrogen center of the phosphazene anion cannot effectively attack the carbocation to form the diphosphazene, instead the oxygen center of the anion attacks the carbocation reforming **5**. The importance of the formation of a dioxolane stabilized carbocation was tested by subjecting (4-oxybutyl methacryl)pentachlorocyclotriphosphazene (**6**) to the harshest rearrangement conditions. The ^{31}P NMR spectrum showed no change during the course of the experiment. The lack of rearrangement of **6** points to the importance of stabilizing effect of the carbonyl oxygen on the carbocation. In the case of **6** the intermediate formed would be a highly strained seven-membered 1,3-dioxepane ring. The general requirements for rearrangement were also tested with (2-oxypropyl methacryl)pentachlorocyclotriphosphazene (**7**) and (1-methyl-2-oxyethyl methacryl)pentachloro-cyclotriphosphazene (**8**). Both were found to have similar rates of rearrangement compared to **1**. Both meet the criteria of being able to form ion pairs and allow for the formation of a dioxolane stabilized carbocation. The hexa(2-oxyethyl methacryl)cyclotriphosphazene (**9**) also undergoes thermal rearrangement under the same experimental conditions used to study the rearrangement of **1**.

In conclusion, a detailed mechanism of the phosphazene/phosphazane rearrangement for **1** has been established. The proposed mechanism allows for rationalization of all of the products formed in the thermolysis of **1** and an understanding of the behavior of related systems.

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