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The Synthesis and ^{31}P NMR Spectral Studies of Cyclophosphazenes

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A modified method for preparing large-scale quantities of pure hexachlorocyclophosphazene ($\text{N}_3\text{P}_3\text{Cl}_6$) and octachlorocyclotetraphosphazene ($\text{N}_4\text{P}_4\text{Cl}_8$), phosphorus pentachloride with ammonium chloride, in the presence of zinc chloride, has been developed. The time of the reaction and the quantities of the catalyst are also studied. It is found that the optimum reaction time is 1.5 h and by-products are remarkably reduced by addition of 10% zinc chloride. As indicated by the ^{31}P NMR spectra, the synthesis and separation of cyclophosphazenes can be accomplished in moderate yield of tetramer (39%) and good yield of trimer (83%).

Keywords Cyclophosphazenes; ^{31}P NMR; pyridine; synthesis; zinc chloride

INTRODUCTION

Phosphazenes, particularly cyclophosphazene, continue to receive considerable commercial interest because of their diverse range of material properties,^{1–3} and so the synthesis of cyclophosphazene has become more and more important.^{4–5} The phosphonitrilic chlorides (PNCl_2)_n

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were first recognized as a homologous series by Stokes,⁶ who separated the hexachlorocyclophosphazene from the products of the reaction of ammonium chloride with phosphorus pentachloride in a sealed tube in the range 150–200°C. This process would finish after 7.5 h. The method of preparation was improved by Schenk and Romer⁷ by using sym-tetrachloroethane as solvent. The synthesis of pure octachlorocyclotetraphosphazene is often accompanied by various preparative difficulties due to separation procedures based on distillation, extraction, or fractional crystallization of mixtures containing $(\text{PNCl}_2)_n$ $n = 3-8$, which is obtained most commonly by the reaction of $\text{PCl}_5 + \text{NH}_4\text{Cl}$ in tetrachloroethane.⁸ Additionally, Becke-Goehring and Lehr⁹ and Yuan et al.¹⁰ describe a direct synthesis of $(\text{PNCl}_2)_4$ in an inert solvent using linear chlorophosphazene $(\text{PCl}_3\text{NPCl}_3)^+ \text{Cl}^-$ and ammonium chloride as starting materials. In their method, pure tetramer $(\text{PNCl}_2)_4$ can be directly prepared with improved yield, while the starting material linear chlorophosphazene $(\text{PCl}_3\text{NPCl}_3)^+ \text{Cl}^-$ is not easily available. In Yuan et al.'s article, they only got tetramer in the presence of anhydrous cobalt(II) chloride.¹⁰

Recently, we have developed a method for direct preparation of the trimer hexachlorocyclophosphazene $(\text{PNCl}_2)_3$ and tetramer octachlorocyclotetraphosphazene $(\text{PNCl}_2)_4$ in chlorobenzene, in the presence of anhydrous zinc chloride. Furthermore, trimer became the main product in 83% yield, when 0.2 mL pyridine was added. According to ^{31}P NMR spectra, the process is finished in 0.5 h, and fewer by-products are produced in comparison to Stoke's 7.5 h method. Moreover, the starting materials, phosphonitrilic chlorides, ammonium chloride, and solvent chlorobenzene, are cheaper and more readily available.

RESULTS AND DISCUSSION

In order to measure for the higher yield of tetramer, the process was followed by ^{31}P NMR spectra as shown in Figure 1 (without catalyst) and Figure 2 (in the presence of ZnCl_2). In Figure 2, the starting material PCl_5 (about -80 ppm) disappeared, while the products $(\text{PNCl}_2)_3$ and $(\text{PNCl}_2)_4$ were observed as new peaks in 20.3 ppm and -6.4 ppm, respectively. Compared to 3 h without a catalyst, phosphorus pentachloride disappeared in 0.5 h with the catalyst. The ^{31}P NMR spectra show that fewer byproducts were produced, and the main products were trimer and tetramer in the presence of catalyst.

Considering the quantity of catalyst, we probed these processes with varying quantities of zinc chloride. These reactions were also studied by ^{31}P NMR. According to the ^{31}P NMR spectra, the yield of trimer

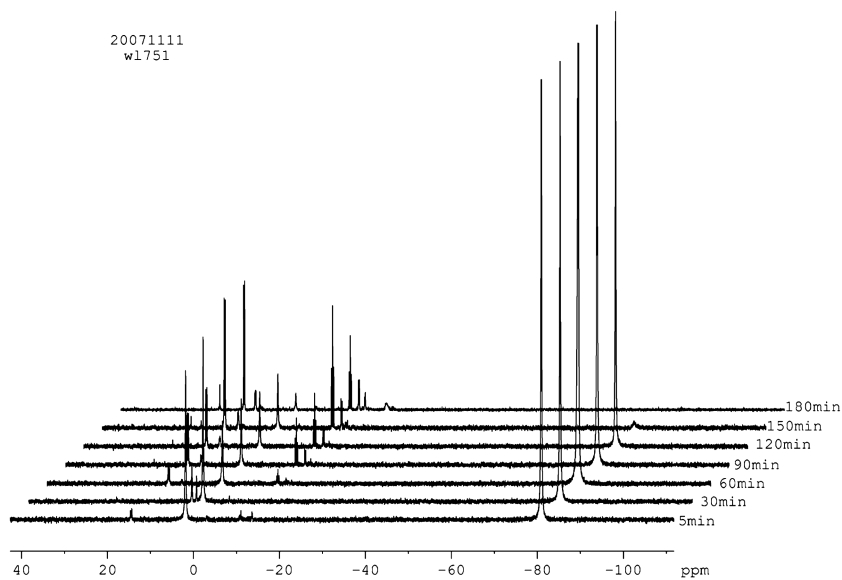


FIGURE 1 The stack ^{31}P NMR spectra of reaction without catalyst.

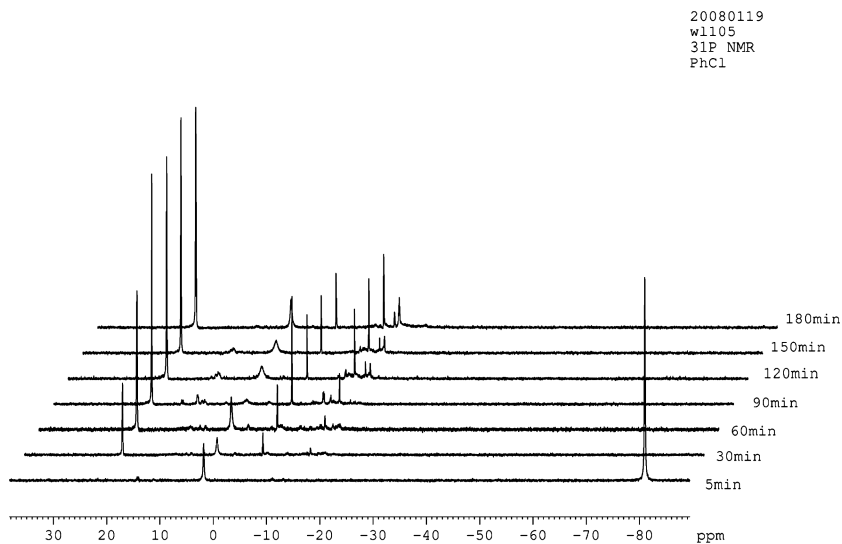


FIGURE 2 The stack ^{31}P NMR spectra of reaction with ZnCl_2 .

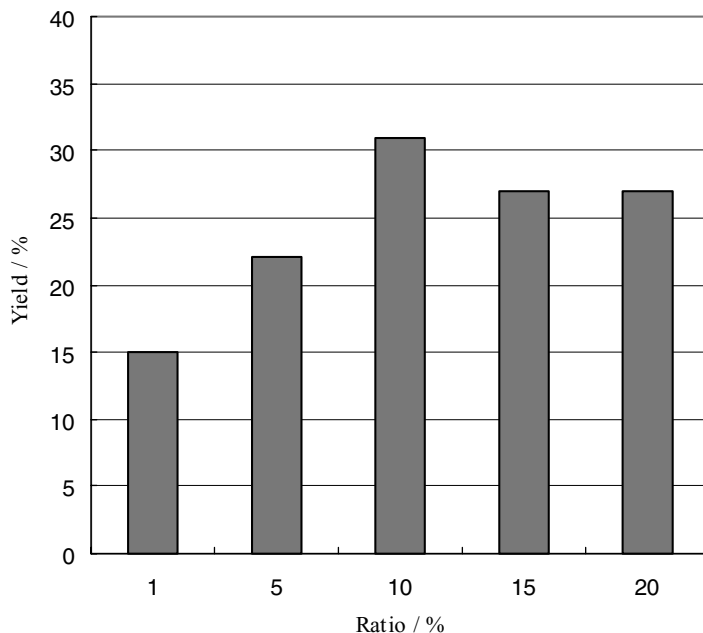


FIGURE 3 Yield of tetramer vs. $\text{ZnCl}_2/\text{PCl}_5$.

was not affected remarkably by the quantities of catalyst and is almost stable in 57% yield. More interesting, the yield of trimer increases to 83% in the presence of 0.02 mL pyridine besides ZnCl_2 . According to ^{31}P NMR spectra, we find that the main product is trimer. The effect of the ratio of $\text{ZnCl}_2/\text{PCl}_5$ on yield of $(\text{NPCl}_2)_4$ is shown in Figure 3. The yield of tetramer first increases to 31% then is reduced to 27% along with the increasing of catalyst. The best condition is the 10% ratio. However, both of the yields are almost invariable when the ratio exceeded 20%.

Furthermore, reaction time was also studied by ^{31}P NMR, on the basis of the ratio 10% of $\text{ZnCl}_2/\text{PCl}_5$. The results were shown in Figure 4. The yield of tetramer first increases, then is unstable as the reaction time is prolonged. Although the trimer is the main product, the yield of tetramer can reach 39% when the reaction time is 1.5 h. More interesting, both of the yields began to decrease when the time exceeded 3 h. The ^{31}P NMR spectra also shows that intensity of the linear byproducts, of which the chemical shift is $-12 \sim -18$ ppm, increases with prolonged reaction time.

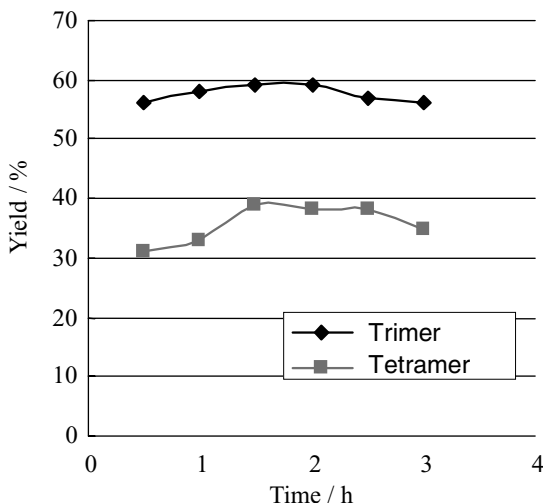


FIGURE 4 Influence of time on yield of cyclophosphazene.

CONCLUSION

The synthesis of cyclophosphazene was investigated in different conditions by ^{31}P NMR. We developed a modified method for preparing larger quantities of pure hexachlorocyclophosphazene ($\text{N}_3\text{P}_3\text{Cl}_6$) and octachlorocyclotetraphosphazene ($\text{N}_4\text{P}_4\text{Cl}_8$) in the presence of zinc chloride. By adding 10% ZnCl_2 , the tetramer can be obtained in a moderate yield of 39% after refluxing for 1.5 h, while the yield of trimer can reach 83% in the presence of 2 mL pyridine.

EXPERIMENTAL

Melting points were measured using a WC-1 microscopic apparatus and were corrected. Infrared spectra were recorded on a Bruker VECTOR22 spectrophotometer in KBr pellets. ^{31}P NMR spectra are measured by a Bruker AMX 400 MHz with 85% H_3PO_4 as external reference. Solvents used are purified and dried by standard procedures.

Method A

Ammonium chloride (0.012 mol, 0.642 g), chlorobenzene (15 mL), and anhydrous zinc chloride (0.0005 mol) were added to a three-neck flask, and then heated to refluxing for 5 min. Then phosphorus pentachloride (0.01 mol, 2.08 g) was added in batches. The mixtures were kept

refluxing for 3 h. The excess of ammonium chloride and the catalyst were filtered off from the resulting brown solution. After the pale brown filtrate was removed by distillation under reduced pressure, 1.83 g of brown cyclophosphazene was obtained, which was mainly tetramer and trimer. The solid mixture first was repeated and extracted with light petroleum (30 mL \times 4), and then the petrol solution was extracted in batches with 98% sulfuric acid (20 mL \times 3). Tetramer could be obtained through concentrating the remaining petrol solution. Extracting the precipitated tetramer with fresh petrol and 0.71 g (yield 16%) white crystal was obtained. M.p. 121–122°C (lit.:123.8°C [11]). IR, 1300 cm^{-1} (P=N), 778 cm^{-1} (P-N), 598 cm^{-1} (P-Cl). ^{31}P NMR: -6.4 ppm in THF (lit. -7.2ppm [12]). Trimer was dissolved preferentially by the acid and was recovered from it by diluting the acid solution to approximately 60% sulfuric acid and back-extracting the precipitated trimer with petrol. Upon concentrating this solution, 1.67 g (yield 57%) trimer was obtained. Mp: 112–113°C. IR, 1210 cm^{-1} (P=N), 874 cm^{-1} (P-N), 600 cm^{-1} (P-Cl), ^{31}P NMR: 20.3 ppm in THF, the same as in the literature.¹²

Method B

Similar to method A, 0.02 mL pyridine was added as a catalyst besides zinc chloride. The mixture was dealt with the same as in method A. At last, 2.43 g trimer (yield 83%) was obtained.

REFERENCES

- [1] V. Chandrasekhar and A. Athimoolam, *Org. Lett.*, **4**, 2113 (2002).
- [2] E. W. Ainscough, A. M. Brodie, A. B. Chaplin, J. A. Harrison, and C. A. Otter, *Inorg. Chem.*, **46**, 2575 (2007).
- [3] H. R. Allcock, S. Al-Shali, D. C. Ngo, K. B. Visscher, and M. J. Parvez, *J. Chem. Soc., Dalton Trans.*, 3549 (1996).
- [4] W. Michael and W. R. Herbert, *Chem. Rev.*, **94**, 1163 (1994).
- [5] H. R. Allcock and J. L. Desorcies, *Polyhedron*, **61**, 119 (1987).
- [6] H. N. Stokes, *Am. Chem. J.*, **19**, 782 (1897).
- [7] M. Becke-Goehring and W. Lehr, *Z. Anorg. Allg. Chem.*, **325**, 278 (1963).
- [8] J. E. Proctor, N. L. Paddock, and H. T. Searie, *Chem. Abstr.*, **55**, 21672 (1961).
- [9] M. Becke-Goehring and W. Lehr, *Z. Anorg. Allg. Chem.*, **327**, 128 (1964).
- [10] F. L. Yuan, Y. J. Zhu, J. G. Zhao, B. Zhang, and D. X. Jiang, *Phosphorus, Sulfur, and Silicon*, **176**, 77 (2001).
- [11] M. Kouril, L. Mezink, and L. Dlabaja, *Collect. Czech. Chem. Commun.*, **53**, 1239 (1988).
- [12] L. G. Lund and N. L. Paddock, *J. Chem. Soc.*, 2542 (1960).