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Cyclotriphosphazatriene Derivatives. XXIX. Reaction of Cyclophosphazatriene Dichloride With Sodium Hydrosulfide

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Cyclotriphosphazatriene Derivatives. XXIX. Reaction of Cyclophosphazatriene Dichloride with Sodium Hydrosulfide

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ABSTRACT

The chlorine substitution reaction of trimeric dichlorocyclophosphazene with sodium hydrosulfide has been examined. The reaction proceeded easily in dioxane and THF solutions. The reaction product, which had the chemical composition $P_3N_3S_6H_6$, was examined by ^{31}P-NMR and IR spectroscopy. Further, it is suggested that the product was polymerized by heating with hydrogen sulfide, and the polymer (PNS) was formed.

INTRODUCTION

Trimetathiophosphimic acid was first prepared by Stokes in 1895 [1]. Recently, several studies [2] have been reported on the preparation of tri- and tetrametathiophosphimic acid by the reaction of cyclophosphazatriene and cyclophosphazatetraene chlorides with hydrogen sulfide, and the reaction of cyclophosphazatriene in dry pyridine with thiourea or ammonium thiocyanate, followed by treatment with EtOH and HCl at pH 1 ~ 2, gave trimetathiophosphimic acid.

Alternatively, phosphorus thionitride $(PNS)_n$ has been prepared by Glatzel [3] and Stock et al. [4] by ammonolysis of phosphorus pentasulfide. In this paper, the chlorine substitution reaction of trimeric dichlorocyclophosphazene with sodium hydrosulfide is investigated, and the structure and polymerization of the product are reported.

EXPERIMENTAL

Trimeric dichlorocyclophosphazene $(PNCl_2)_3$ was prepared by the reaction of phosphorus pentachloride (PCl_5) with ammonium chloride (NH_4Cl). Pure trimer can be obtained after several fractional crystallizations from petroleum.

Sodium hydrosulfide (NaSH) was prepared by the reaction of sodium ethoxide (EtONa) with hydrogen sulfide (H_2S) in ethanol. The sodium hydrosulfide was purified by several recrystallizations from ethanol and ether.

IR spectra were obtained for the products using the pressed KBr disk technique. ^{31}P-NMR spectra were determined for the products using nitromethane solvent at 25°C for 24 MHz.

RESULTS

Trimeric dichlorocyclophosphazene, 3.36 g (0.01 mole), and sodium hydrosulfide, 3.48 g (0.06 mole), were reacted together in 25 ml of dioxane at 30°C for 24 hr. Then the reaction mixture was separated by filtration. The residue thus obtained was examined by x-ray diffraction analysis, and the results are shown in Fig. 1. It was concluded that a part of the residue was sodium chloride.

The same reaction was run in several solvents at 30°C for 24 hr. The conversion was determined by the Volhard method, and the results are given in Table 1. The reaction was also run in dioxane

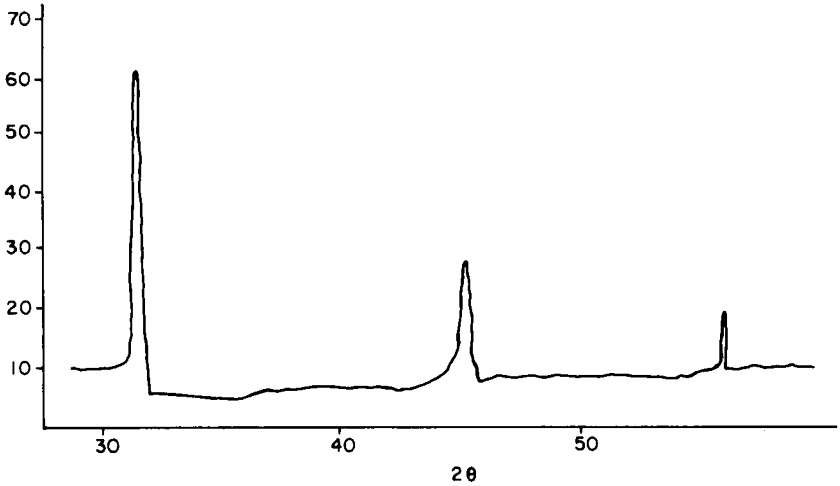


FIG. 1. X-ray diffraction analysis.

under various experimental conditions. The results are shown in Tables 2 and 3, and Fig. 2.

After termination of the reaction, the filtrate was evaporated under reduced pressure. Pure product was obtained by reprecipitation from an ethanol/carbon tetrachloride mixture. The chemical analysis of the product is given in Table 4. IR and ^{31}P-NMR spectra of the product are shown in Figs. 3 and 4, and the DTA curves are shown in Fig. 5.

The gas formed by heating at 162°C was examined by gas chromatography. It was found to contain large amounts of hydrogen sulfide.

The heat-treated material was investigated by IR spectra. It showed a diffuse band in the 1250 cm^{-1} region and the band characteristic for the S–H group in the range of 3450 to 3300 cm^{-1} had disappeared.

The P–S and P=S frequencies were detected in the region 930 to 980 cm^{-1} and 500 to 540 cm^{-1} [5].

DISCUSSION

Since sodium chloride was detected by x-ray analysis and the product was investigated by IR, ^{31}P-NMR spectra, and chemical

TABLE 1. Reaction Percent Obtained for the Reaction of Phosphazatriene Chloride with Sodium Hydrosulfide in Several Solvents at 30°C for 24 hr

Solvent	Dielectric constant, ϵ	Specific conductivity, μ	Dipole moment, κ	Reaction percent
Methanol	78.5	1.84	4.41×10^{-8}	14.58
Ethanol	24.3	1.68	1.5×10^{-7}	41.58
Acetone	20.7	2.72	5.8×10^{-8}	63.36
Methyl ethyl ketone	18.5	2.75	1×10^{-7}	70.24
Acetonitrile	37.5	3.37	$5{\sim}9 \times 10^{-8}$	57.86
Dioxane	2.21	0.45	5×10^{-15}	86.29
Ether	4.34	1.15	1×10^{-15}	59.05
THF				51.58
Carbon tetrachloride	2.23	0	4×10^{-18}	4.59
Carbon disulfide				3.62
Chloroform	4.8	1.15	1×10^{-19}	3.88
Benzene	2.27	0	1×10^{-15}	3.93
Toluene	2.4	0.39	1.4×10^{-14}	2.62
Nitromethane	35.9	3.17	$5{\sim}9 \times 10^{-8}$	73.91
Cyclohexane	2.02	0	-	3.63
n-Buthylamine	5.3	1.4	-	68.08

TABLE 2. Reaction Percent at Various Temperatures when the Molar Ratio of NaSH to $(NPCl_2)_3$ Was 6

Reaction temp (°C)	Reaction percent
20	74.85
30	86.29
55	75.64
75	70.83

TABLE 3. Relationship between Molar Ratio of $NaSH/(NPCl_2)_3$ and Reaction Percent at 30°C for 24 hr

Molar ratio $NaSH/(NPCl_2)_3$	Reaction percent
6	86.27
10	87.35
12	88.00
18	95.12
24	100.00

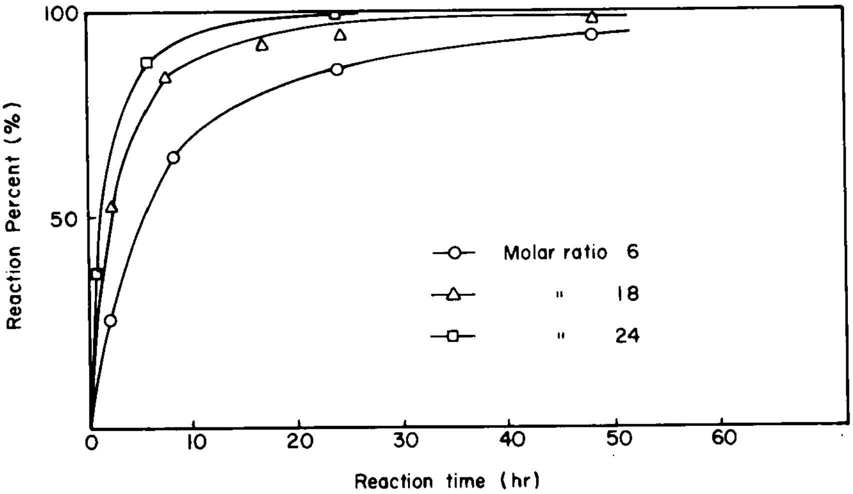


FIG. 2. The relationship between time and reaction percent at 30°C.

TABLE 4. Chemical Analysis of the Product

Chemical compositions	Calcd (%)			Molecular weight	Found (%)			Molecular weight
	P	N	S		P	N	S	
$P_3N_3S_6H_6$	27.78	12.98	59.35	330	28.12	12.81	58.90	359

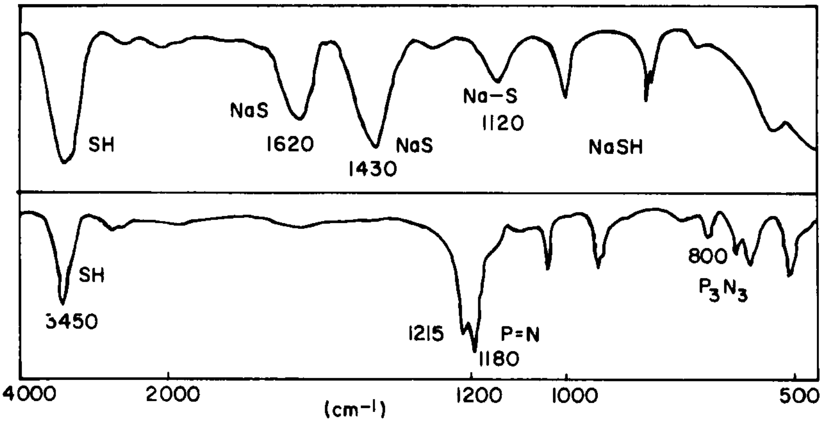


FIG. 3. IR spectra of the product and sodium hydrosulfide.

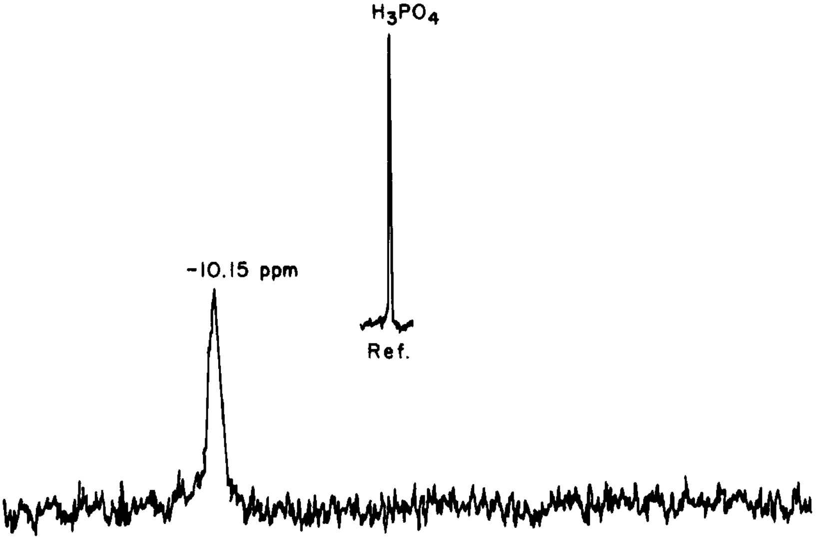


FIG. 4. ^{31}P-NMR spectra of the product.

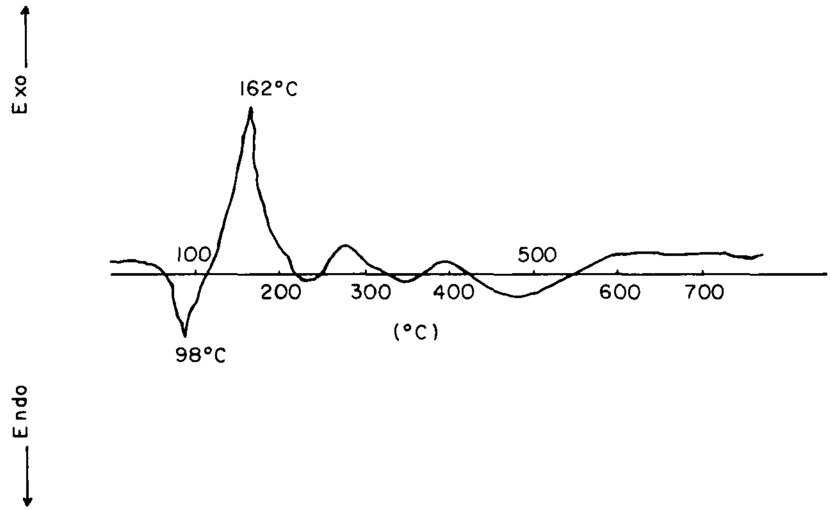


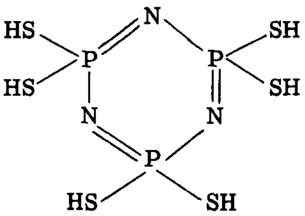
FIG. 5. DTA of the product. In open air, 5°C/min.

analysis, the substitution reaction of the cyclophosphazene with sodium hydrosulfide can be written as

$$(PNCl_2)_3 + 6NaSH \longrightarrow [NP(SH)_2]_3 + 6NaCl$$

I

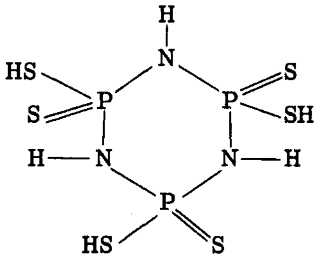
This reaction proceeded readily in dioxane or THF. Structure II is proposed as the structure of the product $[NP(SH)_2]_3$:



II

The product was soluble in polar solvents but not water, and was surprisingly soluble in nonpolar solvents. It had a melting point of about 98°C. On the other hand, it was reported by Yanik and Zheshutko that the product they obtained was soluble in water and not soluble in most organic solvents. Further, the S–H frequency was detected in the range of 2535 to 2485 cm^{-1}. This absorption is more probable for an N–H group than for S–H [6].

It is suggested that the product obtained by Yanik and Zheshutko [2] was Structure III.



III

When Structure II was heated at 162°C, hydrogen sulfide was evolved and the product has a band in the region 500 to 550 cm^{-1}, corresponding to the P=S group. It is proposed that this resulted from condensation polymerization of Structure II:

$$n[NP(SH)_2]_3 \longrightarrow [PNS]_n + nH_2S$$

IV

Product IV did not melt, was stable to over 400°C, and was insoluble in most organic solvents and water. It was therefore very similar in properties to the compound $(PNS)_n$ obtained by Glatzel [3].

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