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Studies on Phosphorus-Containing Polymers. IX. On the Reaction of Triphosphonitrilic Chloride with Ethylene Glycol

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Studies on Phosphorus-Containing Polymers. IX. On the Reaction of Triphosphonitrilic Chloride with Ethylene Glycol

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ABSTRACT

This paper is concerned with the reaction of triphosphonitrilic chloride and ethylene glycol, and with the properties of the triphosphonitrilic glycol ester obtained. The reaction studied was a dehydrochlorination of triphosphonitrilic chloride with glycol by heating. The ester obtained from the reaction could be further hydrolyzed to produce ammonium chloride and ethylene chlorohydrin. It thus clarified the reaction mechanism of triphosphonitrilic chloride with ethylene glycol.

INTRODUCTION

The reaction of triphosphonitrilic chloride (TPNC) with saturated aliphatic monohydric alcohols was described in previous reports [1, 2]. A similar reaction is expected to occur between TPNC and saturated aliphatic dihydric alcohols. No report on the products resulting from the reaction has been published. The purpose of our present study is to describe the properties of the products resulting from the reaction of TPNC with ethylene glycol, and to throw light on the

mechanism of the reaction. This article describes some experimental results obtained by the thermal condensation of TPNC with a glycol, involving the separation of hydrogen chloride.

EXPERIMENT

Synthesis of TPNC and Purification of Reagents

Synthesis of TPNC

The TPNC was synthesized by the technique mentioned in a previous paper [3].

Analysis: Calculated for $(PNCl_2)_3$: N, 12.08%; molecular weight, 348. Found: N, 12.13%; molecular weight, 339.

Ethylene Glycol

A commercial preparation of ethylene glycol was purified according to a conventional method. After distillation, the distillate fraction with a boiling point range between 195-198° C was dehydrated with anhydrous sodium sulfate and used for later experiments.

Xylene

A commercial preparation of xylene was freed from thiophene by concentrated sulfuric acid, washed with water, and dehydrated with calcium chloride. Then distillation was carried out, and the distillate fraction with a predetermined boiling point range was used for later experiments.

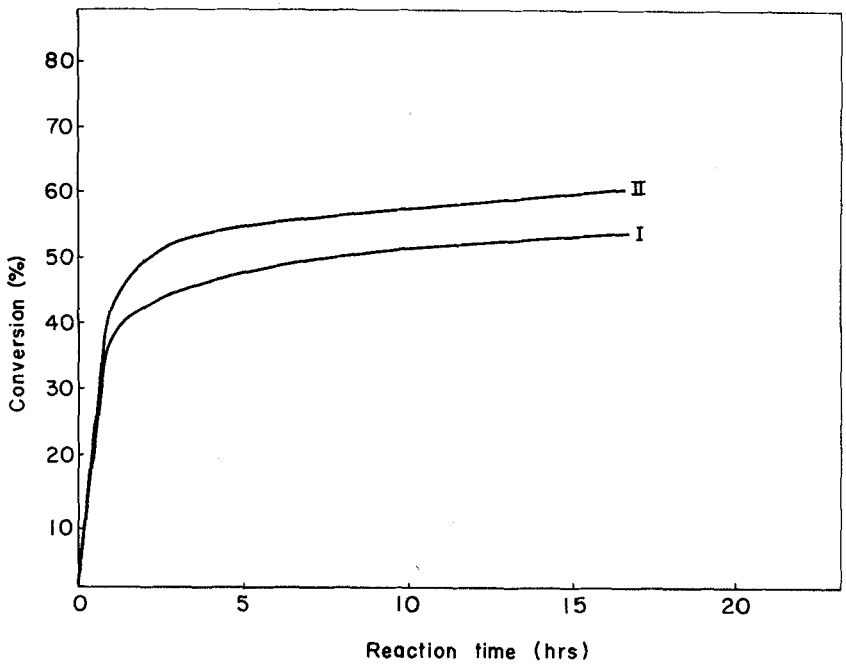
Conversion of TPNC and Ethylene Glycol

One gram of TPNC was placed in a four-necked flask fitted with a thermometer, a stirrer, and a reflux condenser. It was mixed with glycol for a predetermined time in the presence of a solvent. The resultant HCl was extracted with water, and its content determined by the Volhard method. The percentage by weight of HCl found was taken as the conversion (cf. Fig. 1).

Reaction of TPNC with Ethylene Glycol

For the reaction, the amounts of glycol and TPNC were in molar ratios (functional group ratio) of 2, 3 and 4. Our description here will use Experiment 3 with a molar ratio of 4 as an example.

TPNC and glycol were placed in a four-necked flask fitted with a thermometer, a stirrer, and a reflux condenser. They were thoroughly



I Condensation with the separation of hydrogen chloride (molar ratio, 2)
II Condensation with the separation of hydrogen chloride (molar ratio, 4)

FIG. 1. Condensation of triphosphonitrile chloride and ethylene glycol.

mixed and then refluxed for a fixed time. During the reaction, crystals came out. The reaction mixture was filtered to separate the crystals and the liquid material. The crystals were recrystallized from water. The liquid material was distilled under ordinary pressure. The distillate was studied with a small size Hempel's fractionating column while the residue was subjected to determination.

RESULTS AND DISCUSSION

Thermal Condensation with the Separation of Hydrogen Chloride

The reaction was carried out according to the technique described in the preceding paragraph under conditions which, together with the results obtained by the reaction, are given in Table 1.

Table 1. Conditions and Results of Reaction

Exp. No.	TPNC		Glycol		Molar ratio of Glycol / TPNC	Reaction		Products			
								Crystals	Liquid		
	(g)	(mol)	(g)	(mol)		Temp. (°C)	Time (hr)	(g)	Total (g)	Distillate (g)	Residue (g)
1	34.8	0.10	75.0	1.20	2	100	17	11.0	—	100~160°C 38.0	31.5
2	17.4	0.05	56.0	0.90	3	100	17	5.0	54.0	80~165°C 28.2	19.0
3	17.4	0.05	75.0	1.20	4	100	20	1.2	83.0	100~175°C 53.5	26.0

Table 2. Analysis of the crystals

Exp. No.	Molar ratio of Glycol/TPNC	Found	
		N (%)	Cl (%)
1	2	26.98	64.61
2	3	26.91	66.56
3	4	26.36	65.85

The reaction products in Experiments 1 to 3 in Table 1 are as follows.

Crystals Coming Out during the Reaction

Cl^-, PO_4^{3-} and NH_4^+ were qualitatively detected in the crystalline solid and the amounts of N and Cl determined. The results are given in Table 2.

The calculated contents of N and Cl in ammonium chloride are 26.2 and 66.3%, respectively. Accordingly, the crystalline solid may consist mainly of ammonium chloride and a small amount of phosphoric acid and ammonium phosphate.

Distillate

The distillate of Experiment 3 (molar ratio of the reactants: 4) was used for determining the constituents. The study was made with a small Hempel's fractionating column. The results are plotted in Fig. 2. By measuring the physical properties, each of the distillate fractions corresponding to plateaus I, II, and III in Fig. 2 were identified as the azeotrope of ethylene chlorohydrin and water, ethylene chlorohydrin,

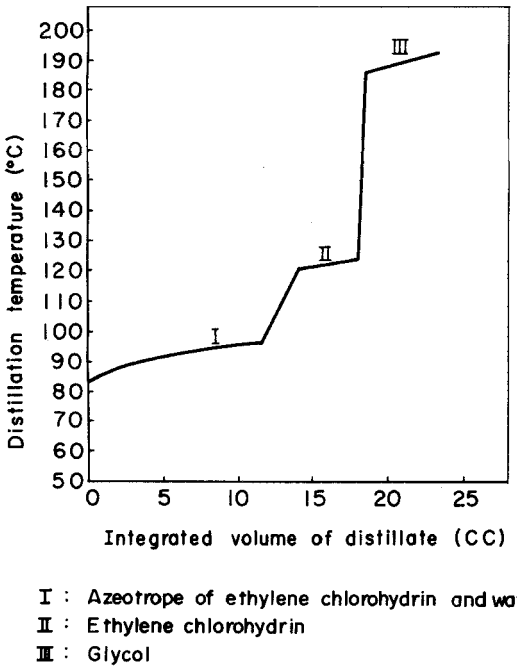


FIG. 2. Distillation curve when the liquid distillate was rectified.

and glycol, respectively. Table 3 lists the results compared with the literature values.

Residue

The residues in Experiments 1 to 3 are all a yellow-brown semi-transparent plastic material soluble in warm water. Since PO_4^{3-}, Cl^-, and NH_4^+ were detected, it is probable that they contain water-soluble ammonium chloride and phosphoric acid. However, the residues were not washed off thoroughly because they are soluble in warm water. This may be the reason for the varying results of their chemical composition as given in later experiments.

As an example, elementary analysis of the residue in Experiments 3 showed the following contents: N, 5.90%; P, 16.39%; Cl, 1.15%. From this result it is probable that triphosphonitrilic glycol ester contained unsubstituted chlorines–$P_3N_3(OCH_2 \cdot CH_2 \cdot OH)_x \cdot Cl_{6-x}$ may have been formed by the condensation of TPNC with glycol (calculated contents for $P_3N_3(OCH_2 \cdot CH_2 \cdot OH)_6$: N, 8.40%; P, 18.56%). It is

Table 3. Measurements relative to the rectification

Fraction No. Name of component	Distillation Temp (°C)		Specific Gravity (d_4^{20})		Refractive index (n_D^{20})	
	Literature value	Found	Literature value	Found	Literature value	Found
I : Azeotrope of ethylene chlorohydrin and water	96.0	95~97	1.097	1.100	—	1.3960
II : ethylene chlorohydrin	128.6	122~124	1.207	1.202	1.4438	1.4430
III : glycol	197.2	197~200	1.113	1.118	1.4274	1.4340

Notes : 1) Each specific gravity was of measurement with a specific gravity bottle.
2) Each refractive index was obtained with an Abbe's refractometer.
3) Literature values in Table were cited from the book "YOUZAI (Solvents)" by Tsutomu Kuwata.
(MARUZEN CO., LTD., TOKYO JAPAN 1951)

an incomplete substitution product of TPNC. Therefore, further study of such a technique, in particular the reaction conditions and the procedure, would permit preparation of the hexa-substituted ester. Additional study of this question is intended.

As described above, the crystalline solid could be considered as ammonium chloride, the distillates as ethylene chlorohydrin and water, and the residue as $P_3N_3(OCH_2{\cdot}CH_2{\cdot}OH)_xCl_{6-x}$. This leads us to infer the following reaction mechanism:

At the first stage of the mechanism a condensation occurs with the separation of hydrogen chloride:

$$P_3N_3Cl_6 + xC_2H_2(OH)_2 \longrightarrow P_3N_3(OCH_2{\cdot}CH_2{\cdot}OH)_x{\cdot}Cl_{6-x} + xHCl \quad (1)$$

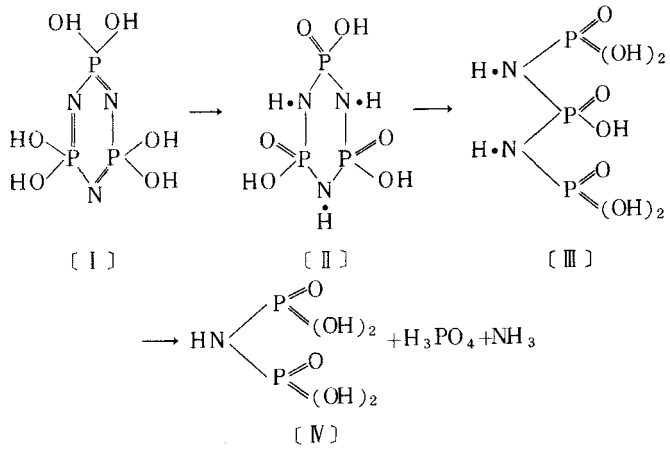
where x has a value of from 1 to 6.

Subsequently, the secondarily produced hydrogen chloride reacts with surplus $C_2H_4(OH)_2$ to form ethylene chlorohydrin and water:

$$HCl + C_2H_4(OH)_2 \longrightarrow ClCH_2{\cdot}CH_2OH + H_2O \quad (2)$$

The hydrogen chloride and water formed according to Eqs. (1) and (2) react with a part of the triphosphonitrilic glycol ester, resulting in the production of triphosphonitrilic acid, $P_3N_3(OH)_6$ (I).

According to Stokes [4-6], Compound (I) is unstable and can be converted by an intramolecular rearrangement into imidotriphosphonitrilic acid (II), which in turn decomposes in an acid environment through diimidotriphosphoric acid (III) to imidodiphosphoric acid (IV) to form phosphoric acid and ammonia as end products.



〔I〕 〔II〕 〔III〕 〔IV〕

It is inferred that in our experiments the same process was accomplished, and the end products react with the by-product hydrogen chloride to form ammonium chloride and ammonium phosphate which are crystallized during the reaction. Therefore, on the basis of the results, the mechanism of thermal condensation with the separation of hydrogen chloride has been established.

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