

PREPARATION, PROPERTIES AND MOLECULAR STRUCTURE OF HEXAPHENOXY-CYCLOTRIPHOSPHAZENE, I.

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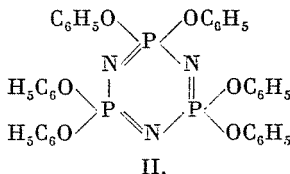
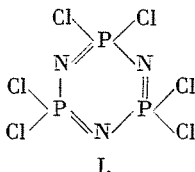
J. NAGY, I. BARTA and J. RÉFFY

Department for Inorganic Chemistry, Polytechnical University, Budapest

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Phosphazenes are of interest for several reasons. Among their advantageous properties good heat resistance and stability are the most important. Our experiments were carried out on hexaphenoxy-cyclotriphosphazene (II), a derivative of hexachloro-cyclotriphosphazene.

(I.)



Substituted phosphazene compounds can be divided into two groups according to whether the compound is cyclic or not. Derivatives preserving the cyclic structure are oily. Our present paper deals with a compound of this type.

Phenoxy phosphazenes were already prepared by LIPKIN [1] in 1940 by boiling hexachloro-cyclotriphosphazene with sodium-phenolate in an aqueous medium. The reaction time was 40 hours. The final product was a tarry, oily substance of a non definable composition, since the long treatment with alkali most probably led to the breaking of the ring.

Aryloxy derivatives of cyclophosphazenes were under similar conditions also prepared by BROWN [2]. His attempts to purify the products by distillation have failed, since the product became resinous under the conditions of the distillation (320°C, some Hgmm pressure), and no distillation product could be obtained.

A suspension of sodium-phenolate in toluene was allowed to react with a solution of hexachloro-cyclotriphosphazene in benzene, and a product corresponding to the formula $P_3N_3(OC_6H_5)_6$ was obtained by YOKOYAMA [3], a Japanese research worker. Some data of the product:

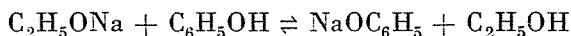
Boiling point:	127—130°C, at 13 Hgmm
n_D^{20} :	1.5802—1.5818
d_4^{20} :	1.4076—1.4083

Taking the above said into consideration the preparation of hexachlorocyclotriphosphazene seemed to be the most advantageous in water-free medium. In order to obtain a stable product of well defined composition a suitable distillation method had to be used to prepare the pure compound.

In our experiments two methods have been used for the preparation: in homogeneous and heterogeneous medium.

Reaction in homogeneous medium

A solution of phenol in water-free ethanol was added to a solution of sodium-ethylate in the same solvent. Phenol, as an acid, forms a salt with the base NaOC_2H_5 in an alcoholic medium:

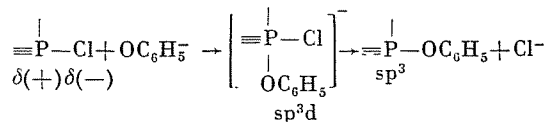


Sodium-phenolate dissociates as follows:



A solution of $\text{N}_3\text{P}_3\text{Cl}_6$ in water-free ethanol was added to the solution of sodium-phenolate prepared as described above.

Phenolate ion reacts with the P—Cl bond in a nucleophilic SN_2 mechanism reaction:



Na^+ and Cl^- ions form NaCl , which precipitates because of its low solubility in ethanol. It is disadvantageous, however, that sodium-phenolate undergoes solvolysis in the ethanolic medium, so also ethylate ions can be present besides phenolate ions, which can also form a bond with phosphorus atoms, so the product is not homogeneous: contains also ethoxy groups besides phenoxy groups.

Because of the above stated the use of alcohol as solvent is not favourable. On the other hand, it seems to be very good for preparing the ethoxy derivative. A similar method was used for preparing hexamethoxy-cyclotriphosphazene with sodium-methylate, using water-free methanol as solvent.

For the preparation of the hexaphenoxy derivative a solvent was sought for, that was inert and therefore did not interfere with the reaction. Xylene was found to be good in this respect. Since sodium-phenolate did not dissolve in xylene, the reaction was carried out in heterogeneous medium.

A solution of hexachloro-cyclotriphosphazene in xylene was added to a suspension of sodium-phenolate in water-free xylene without heating under stirring. The viscous suspension gradually became easy to stir, while sodium-chloride precipitated in the form of fine, powder-like grains, and the mixture turned yellow. This process only lasted for 15 minutes. The mixture was then stirred for 2 more hours, while the temperature was gradually raised to the boiling point of xylene.

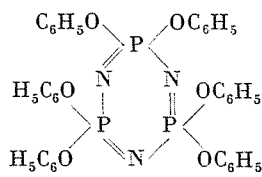
The precipitate was filtered from the cooled mixture, thus a clear solution of hexaphenoxy-cyclotriphosphazene in xylene was obtained. The solvent was distilled off, and the pure product was obtained. The product was a dark-yellow viscous oil. Hexaphenoxy-cyclotriphosphazene could not be purified by the usual distillation method since it became resinous under the given experimental conditions (200°C, 0.01 Hgmm pressure).

It could only be purified by a quick film-distillation, at 90°C, 0.01 Hgmm pressure.

Physical- chemical study of hexaphenoxy-cyclotriphosphazene

Table 1

Data for the product

	Molecular weight		d_4^{20}	n_D^{20}	ϵ		Freezing point °C
	Measured*	Calculated			25°C	50°C	
	673—712	693	1.3369	1.5920	5.68	5.62	+2.0

* Molecular weight was determined by ebullioscopic method, in carbon-tetrachloride.

The viscosity of the product was determined with Ostwald's modified viscosimeter between 25 and 155°C, at every 10°C. Temperature dependence of the viscosity is shown in Figs. 1. and 2.

The temperature coefficient of viscosity (VTC) was determined by means of the following equation:

$$VTC = \frac{\eta_{37.8^\circ C} - \eta_{98.9^\circ C}}{\eta_{37.8^\circ C}} = 0.96$$

where

$\eta_{37.8^\circ C}$ is the viscosity at 37.8°C in centistokes units

$\eta_{98.9^\circ C}$ is the viscosity at 98.9°C in centistokes units.

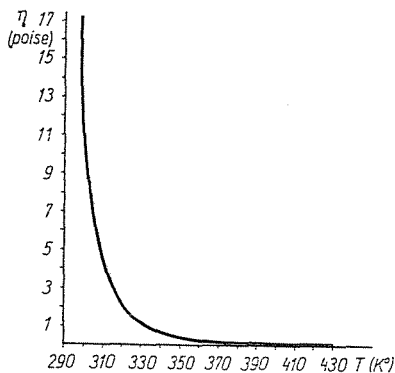


Fig. 1. Temperature dependence of the viscosity of hexaphenoxy-cyclotriphosphazene

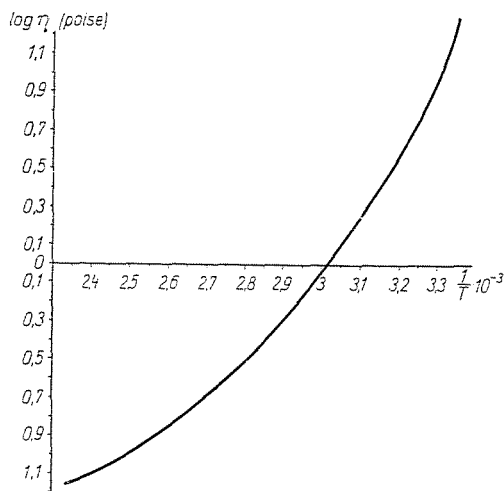


Fig. 2. Logarithm of viscosity of hexaphenoxy-cyclotriphosphazene plotted against the reciprocal value of temperature

The activation energy (ΔH^*) for the viscosities at various temperatures can be determined as follows:

$$\ln \eta = \frac{\Delta H^*}{RT} + \ln \eta_\infty \quad (1)$$

from which

$$\eta = \eta_\infty \cdot e^{\frac{\Delta H^*}{RT}} \quad (2)$$

Differentiating equation (2) by T

$$\frac{d\eta}{dT} = -\eta_\infty e^{\frac{\Delta H^*}{RT}} \cdot \frac{\Delta H^*}{RT^2} \quad (3)$$

Substituting η from equation (2) into equation (3):

$$\frac{d\eta}{dT} = -\eta \frac{\Delta H^*}{RT^2} \quad (4)$$

from which

$$\Delta H^* = -RT^2 \frac{d\eta}{dT} \cdot \frac{1}{\eta}$$

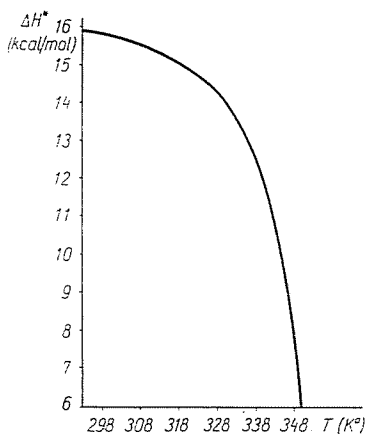


Fig. 3. Temperature dependence of the activation energy of viscosity of hexaphenoxy-cyclotriphosphazene

Calculating ΔH^* energies of viscosities for viscosities measured between 25 and 75°C (the measurement being most accurate in this interval), and plotting them against T the diagram presented in Fig. 3 was obtained.

Resistance to radiation

Subjecting hexaphenoxy-cyclotriphosphazene to a radiation dose of $3 \cdot 10^3$ MRtg, only a slight turbidity was observed, but no change in its properties occurred.

Thermoanalysis

One of the most remarkable properties of phosphazenes is their high heat-resistance. Thermoanalytical measurements were carried out in order to study this property.

For the purposes of comparison the derivatograms of the hexachloro-compound and hexamethoxy-cyclotriphosphazene were also taken besides that of hexaphenoxy-cyclotriphosphazene.

The apparently low temperature of decomposition for hexachloro-cyclotriphosphazene is due to the weight decrease caused by sublimation. This is also proved by the DTA curve indicating an endothermic process, while the

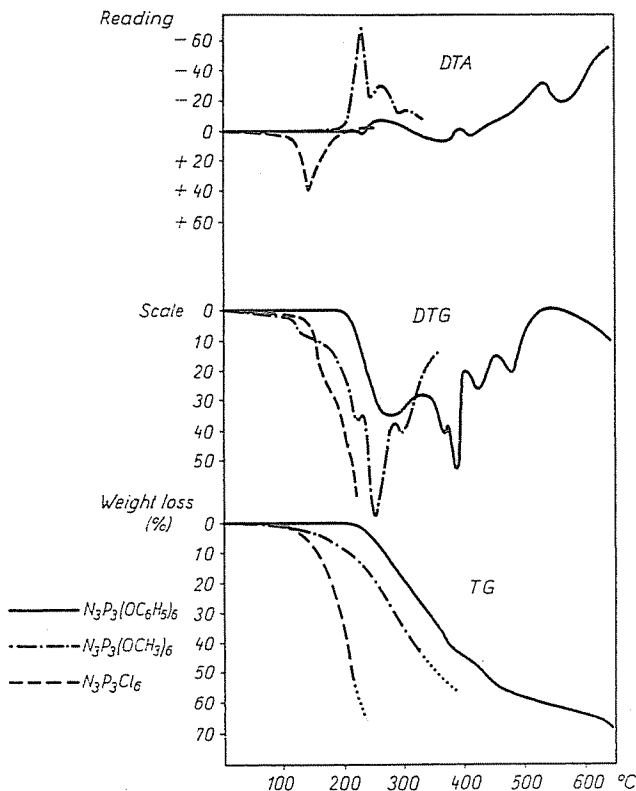


Fig. 4. Derivatograms of cyclotriphosphazene derivatives

exothermic peaks on the DTA curves of the other two compounds are due to decomposition processes.

This measurement, together with others, proves the high stability of hexaphenoxy-cyclotriphosphazene.

The liquid compound preserves its oily character within wide temperature limits. It does not take a crystalline form even at low temperature, no melting point can be observed, only a freezing point. This is due to the steric extensiveness of the aromatic groups, since no complete order can be attained

even by rotation. The hexachloro derivative has a well defined melting point (114°C).

The above said are supported by the fact that the plot $\log \eta - \frac{1}{T}$ deviates from the straight line, and by the strong temperature dependence of the activation energy of viscosity. The activation energy of viscosity reaches its maximum near to the freezing point according to the diagram.

The great difference between the thermal stabilities of the hexaphenoxy and hexamethoxy derivative, and also the high resistance to radiation of hexaphenoxy-cyclotriphosphazene leads to the question whether a conjugation occurs between the benzene and phosphazene aromatic rings or not. This question can only be answered on the basis of thorough molecular structural studies, the results of which will also be published.

Experimental

I. Preparation of hexaphenoxy-cyclotriphosphazene in water-free ethanol

200 ml water-free ethanol was poured into a three-necked flask equipped with a reflux cooler with a tube filled with CaCl_2 on the top, with mercury sealed stirrer and with a dropping funnel, then 14 g finely ground sodium metal was added during stirring and cooling. After no more gaseous hydrogen was produced, a solution of 38 g freshly distilled phenol in 100 ml water-free ethanol was added through the dropping funnel. After cooling a solution of 20 g of hexachloro-cyclotriphosphazene in 150 ml ethanol was added under stirring. The heat produced during the reaction raised the temperature to the boiling point, while the white salt began to precipitate and the solution turned yellow.

The mixture was heated to the boiling point and kept at this temperature for 1 hour. After cooling the precipitated NaCl was filtered and the ethanol distilled off the filtrate.

The oil left back was dissolved in ether and shaken with salted water to obtain good separation. The unreacted phenol which was possibly present was eliminated by washing with NaHCO_3 solution. After distilling the ether off, the oil was clarified with active carbon and filtered on a G4 sintered glass filter. A golden, clear oil was obtained.

Refraction index of the product:

$$n_D^{25} = 1.5580 \text{ (literary date: 1.5802)}$$

Refractive index of hexaethoxy-cyclotriphosphazene $n_D^{25} = 1,4804$ (literary date).

The above said also prove that also ethoxy groups had entered the ring, so the refractive index of the product is lower than that of pure hexaphenoxy-cyclotriphosphazene.

II. Preparation of hexaphenoxy-cyclotriphosphazene in heterogeneous medium

16.6 g (0.72 g atoms) sodium metal suspended in 500 ml water-free xylene was placed into a 1.5 l three-necked flask equipped with a reflux cooler, dropping funnel, mercury sealed stirrer and CaCl_2 tube. Then a solution of 68.0 g (0.72 g moles) phenol in 150 ml water-free xylene was added dropwise under vigorous stirring. Sodium reacted with phenol producing a gaseous hydrogen and a very fine suspension of sodium-phenolate was formed. Then a solution of 34.8 g (0.1 g mole) hexachloro-cyclotriphosphazene in 200 ml water-free xylene was added to the suspension under stirring. The mixture became hot, and white, powder-like and quickly settling NaCl was produced in the place of the thick suspension of sodium phenolate, and the mixture became yellow.

The mixture was then heated to the boiling point of xylene by means of an oil bath and kept at this temperature for 2 hours.

The salt was filtered after cooling, the xylene distilled off, and the oily product left back dissolved in ether and washed. The etheric solution was allowed to stand overnight with CaCl_2 , then the ether was eliminated by distillation, and the solvent traces which might possibly be present by vacuum distillation. The product was then clarified with active carbon, and filtered on a G4 sintered glass crucible.

The product was a viscous, dark brown oil, which, according to literary data [3], could not be purified by distillation, no distillation product could be obtained even at raised temperature and reduced pressure, the product became resinous, which fact was in concordance with reference [2].

The product could be purified by a quick film distillation, at 90°C temperature and 0,01 Hgmm pressure.

Hexaphenoxy-cyclotriphosphazene purified in this way was a golden, clear oil. Yield: 38%.

$$n_D^{20} = 1,5920 \text{ (literary date: } n_D^{20} = 1,5802\text{)}.$$

Further experiments

For comparison purposes also hexamethoxy-cyclotriphosphazene was prepared from sodium-methylate and hexachloro-cyclotriphosphazene in water-free methanol. The product was a colourless, clear oil of much lower viscosity than that of the hexaphenoxy derivative.

Finally we should like to thank dr. G. Liptay, senior lecturer at the Institute for General Chemistry of our University for his help and useful advice in the thermoanalytical studies.

Summary

1. Optimal conditions for the preparation of hexaphenoxy-cyclotriphosphazene were studied. Halogen atoms of hexachloro-cyclotriphosphazene can best be exchanged for phenoxy groups with sodium-phenolate in water-free media. Water-free alcohol as medium is favourable for ethoxy substitution. A completely uniform product can be prepared in water-free xylene.

2. Physico-chemical and reologic properties of the hexaphenoxy product were studied. The compound preserves its liquid character within a wide temperature range, crystalline structure cannot be obtained.

3. According to thermoanalytical studies, the phenoxy derivative is much more stable than the methoxy one. This has also been proved by irradiation experiments.

References

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Dr. József NAGY }
István BARTA } Budapest, XI. Gellért tér 4, Hungary
József RÉFFY }