HYDROLYSIS OF AMIDOCHLORO-CYCLO-TRIPHOSPHAZENES*

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Received April 14th, 1981

It was found by ^{31}P NMR spectroscopy and paper chromatography that amidochloro-cyclo-triphosphazenes $N_3P_3Cl_4(NH_2)_2$ and $N_3P_3Cl_5NH_2$ undergo hydrolysis in acidic, neutral, and alkaline medium with preservation of their cyclic skeleton to give triphosphazane anions $(NHPO_2)_3^{3-}$. As found spectroscopically, the hydrolysis of $N_3P_3Cl_4(NH_2)_2$ in acidic medium leads initially to formation of an intermediate of the composition $N_3P_3(OH)_4(NH_2)_2$, which speaks for the preferential hydrolytic cleavage of P—Cl bonds compared to exogenic P—NH_2 bonds in the molecule of this compoud.

Halogeno-cyclo-triphosphazenes $(NPX_2)_3$ (X = F, Cl, Br) and a series of their derivatives undergo hydrolysis without cleavage of their six-membered ring in the first stage of the reaction, giving anions of cyclo-triphosphazane acid[1] $(HNPO_2)_3^{3-}$. In the case of hexaamido-cyclotriphosphazene $[NP(NH_2)_2]_3$ we have found, however, that the first step of hydrolysis involves the opening of the phosphazene ring[2]. This finding was confirmed also by other authors[3-6] who studied in detail the formation of individual products during hydrolytic cleavage of the molecule of this amido-cyclo-triphosphazene. Similarly as $[NP(NH_2)_2]_3$, *i.e.* with initial ring opening, there proceeds also hydrolysis of diamido-tetrachloro-cyclotriphosphazene $N_3P_3Cl_4(NH_2)_2$, as reported by Ficquelmont[7,8]. This conclusion has been arrived at on the basis of the finding that hydrolysis of $N_3P_3Cl_4(NH_2)_2$ in neutral or alkaline medium for several weeks does not result in formation of cyclo-triphosphazane anion but it produces chain-like μ-diimidotriphosphate anion, while in acidic medium $N_3P_3Cl_4(NH_2)_2$ undergoes fast hydrolysis to afford phosphoric acid, hydrochloric acid and ammonia.

* From rational reasons and in agreement with majority of publications in the world literature, dealing with inorganic heterocyclic nitrogen-phosphorus compounds, the compounds containing —N=P— bond in the basic skeleton are called phosphazenes and those possesing —N(H)—P— bond are called phosphazanes. For comparative purposes we list here the studied compounds according to the IUPAC nomenclature:

$(PNX_2)_3$ (X = F, Cl, Br)	2,2,4,4,6,6-hexahalogeno-1,3,5-triaza-2λ^5,4λ^5,6λ^5-triphosphorine
$N_3P_3Cl_5(NH_2)$	2-amino-2,4,4,6,6-pentachloro-1,3,5-triaza-2λ^5,4λ^5,6λ^5-triphosphorine
$N_3P_3Cl_4(NH_2)_2$	2,2-diamino-4,4,6,6-tetrachloro-1,3,5-triaza-2λ^5,4λ^5,6λ^5-triphosphorine
$[NP(NH_2)_2]_3$	2,2,4,4,6,6-hexaamino-1,3,5-triaza-2λ^5,4λ^5,6λ^5-triphosphorine
$(HNPO_2)_3^{3-}$	anion of 2,4,6-trihydroxy-2,4,6-trioxohexahydro-1,3,5-triaza-2λ^5,4λ^5,6λ^5-triphosphorine acid.

In the above work[8], Ficquelmont mentions also amido-pentachloro-cyclo-triphosphazene $N_3P_3Cl_5(NH_2)$ and believes that its hydrolysis takes place without ring opening and leads initially to the evolution of hydrogen chloride and formation of the compound $N_3P_3Cl_4(OH)NH_2$. This presumption has not been supported, however, by experimental data. On using paper chromatography, Narath, Lohman and Quimby[9] have found that the compound that was obtained by Ficquelmont[7] by hydrolysis of amidochloro-cyclo-triphosphazene $N_3P_3Cl_4(NH_2)_2$ (and also by hydrolysis of cyclo-triphosphazane $Na_3(HNPO_2)_3$ and regarded to be μ-diimidotriphosphate with chain-like anion, is diimido-cyclo-triphosphate with small admixture of imido-cyclo-triphosphate.

With the aim to prove unambiguously whether the presence of amido groups on one phosphorus atom which is the part of cyclo-triphosphazene skeleton leads to hydrolytic opening of the ring, the hydrolysis of the compounds $N_3P_3Cl_4(NH_2)_2$ and $N_3P_3Cl_5(NH_2)$ has been followed by ^{31}P NMR spectroscopy and paper chromatography.

EXPERIMENTAL

Diamidotetrachloro-cyclo-triphosphazene $N_3P_3Cl_4(NH_2)_2$ was prepared according to Ficquelmont[8], by the reaction of ether solution of $(NPCl_2)_3$ with 25% aqueous solution of ammonia. The compound was obtained in c. 65% yield. Amidopentachloro-cyclo-triphosphazene $N_3P_3Cl_5.(NH_2)$ was obtained in c. 60% yield by the procedure reported by Feistel and Moeller[10] based on the reaction of $N_3P_3Cl_4(NH_2)_2$ dissolved in dioxane with dry hydrogen chloride. Sodium cyclo-triphosphazane $Na_3(HNPO_2)_3.4\,H_2O$ that was used as reference compound for ^{31}P NMR spectroscopy and as test substance for chromatographic analysis, was prepared by hydrolysis of $(NPCl_2)_3$, using the procedure reported by Stokes[11].

The purity of the compounds prepared was checked by elemental analysis and by thin layer chromatography[12], eventually by paper chromatography[13]. The ^{31}P NMR spectrum of diamidotetrachloro-cyclo-triphosphazene was identical to the spectrum of this compound reported by Feistel and Moeller[10] who on the basis of the spectrum concluded that both amido groups in $N_3P_3Cl_4(NH_2)_2$ are geminal, *i.e.* they are attached to the same phosphorus atom.

Amidochloro-cyclo-triphosphazenes $N_3P_3Cl_4(NH_2)_2$ and $N_3P_3Cl_5(NH_2)$ are not soluble in water, similarly as $(NPCl_2)_3$; if, however, these compounds are suspended in aqueous medium, they undergo fast gradual hydrolysis and become dissolved. This hydrolytic process at room temperature has been followed in such a way that at fixed time intervals the sample of liquid phase was taken from the suspension of the corresponding amidochloro-cyclo-triphosphazene in water or from the suspension of this compound in dilute aqueous HCl solutions (pH 1 and 3) or in aqueous NaOH solutions (pH 11 and 13). The samples were then used to chromatographic and spectroscopic identification of hydrolytic products. The amount of the starting amidochloro-cyclo-triphosphazene was taken so that the clear solution after its hydrolysis be nearly saturated with respect to the concentration of hydrolytic products. This corresponded to c. $3{\cdot}5 \cdot 10^{-3}$ mol of amidochloro-cyclo-triphosphazene in 10 cm^3 of water or in 10 cm^3 of diluted HCl or NaOH solution.

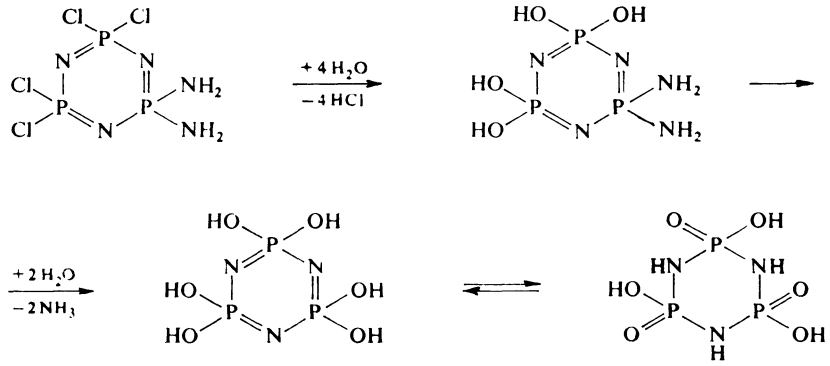
^{31}P NMR spectra were recorded with Varian XL-100 instrument; paper chromatography was used in descent arrangement according to Biberacher[13]. The more detailed description of experimental conditions connected with the application of both above mentioned methods can be find in our earlier work[14].

RESULTS AND DISCUSSION

The results of our experiments show that the hydrolysis of $N_3P_3Cl_4(NH_2)_2$ and $N_3P_3Cl_5(NH_2)$ in acidic, neutral and alkaline medium proceeds first with the retention of cyclic skeleton of these substances. As follows from ^{31}P NMR spectra and chromatographic analysis, $(HNPO_2)_3^{3-}$ anions are formed, similarly as in the hydrolysis of $(NPCl_2)_3$ (ref.[1]). Thus, for example, ^{31}P NMR spectrum of the hydrolysate formed from $N_3P_3Cl_4(NH_2)_2$ on standing the compound in the solution of pH 3 at ambient temperature for two hours shows only one resonance signal with chemical shift − 0·1 ppm, which corresponds to the cyclo-triphosphazane anion $(HNPO_2)_3^{3-}$ in acidic medium. This is in accordance with literature data[14,15] about chemical shift of this compound and results also from comparison of the mentioned spectrum with that of the acid solution of sodium cyclo-triphosphazane $Na_3(NHPO_2)_3$ prepared according to Stokes[11]. The hydrolysate obtained under above conditions from $N_3P_3Cl_4(NH_2)_2$ gives only one spot on chromatogram, as expected, the R_F value of which corresponds to $(HNPO_2)_3^{3-}$ (using $Na_3(NHPO_2)_3.4\ H_2O$ as reference compound).

The more detailed investigation of the hydrolysis of $N_3P_3Cl_4(NH_2)_2$ in acidic medium by means of ^{31}P NMR spectroscopy resulted also in finding hydrolytic intermediate, the formation of which preceeds the formation of cyclo-triphosphazane anion. The formation of this intermediate product is proved by the spectrum of aqueous solution of the hydrolysate obtained from $N_3P_3Cl_4(NH_2)_2$ at ambient temperature immediately after suspending this compound in aqueous HCl solution of pH 1 (Table I).

It is evident that observed signals do not correspond to the starting $N_3P_3Cl_4.(NH_2)_2$ since this compound is water insoluble, as mentioned earlier, and its solution in ether shows ^{31}P NMR spectrum with a triplet (chemical shift 8·5 ppm) and a doublet (chemical shift 18·5 ppm)[10]. The spectrum obtained by us corresponds to the AB_2 spin system and can be interpreted in terms of hydrolytic transformation of two PCl_2 groups (δ = 18·5 ppm in ether solution) in the molecule of $P_3N_3Cl_4.(NH_2)_2$ to give two $P(OH)_2$ groups (chemical shift − 1·58 ppm, the centre of lines 5 and 7, Table I) in aqueous solution, with the possibility of simultaneous protonation of both amido groups on the remaining phoshorus atom (δ = −0·66 ppm in water solution). However, under conditions used, the hydrolytic intermediate formed, *i.e.* diamidotetrahydroxo-cyclo-triphosphazene $N_3P_3(OH)_4(NH_2)_2$, could not be isolated since in very short time both amido groups are converted into two OH groups; at the same time there proceeds also proton transfer from each OH group attached to each phosphorus atom to endogen nitrogen atoms of the ring to form cyclo-triphosphazane acid, as depicted in Scheme 1. The proposed reaction scheme is supported by ^{31}P NMR spectrum of the same solution as in the previous case (Table I), except that the solution was allowed to stand for 5 minutes at ambient temperature. After such a relatively short period, the NMR spectrum shows, in addition to original



SCHEME 1

signals that correspond obviously to $N_3P_3(OH_4)(NH_2)_2$, a relatively strong signal with chemical shift − 0·1 ppm indicating the presence of another cyclo-triphosphazane anion formed by further hydrolysis. As documented by ^{31}P NMR spectra and chromatograms, after two hours, the solution contains cyclo-triphosphazane anions $(HNPO_2)_3^{3-}$ as a sole product. In acidic medium, these anions are further hydrolysed at a slow rate. This hydrolysis involves gradual replacement of NH groups by oxygen atoms, as found earlier chromatographically by Quimby[16] and Pollard and co-

TABLE I

^{31}P NMR spectrum of aqueous solution of the hydrolysate formed from $N_3P_3Cl_4(NH_2)_2$ at ambient temperature immediately after suspending the compound in HCl solution of pH 1

Signal No	Chemical shift	
	Hz	ppm
1	−9	−0·22
2	−18	−0·44
3	−27	−0·66
4	−31	−0·76
5	−60	−1·48
6	−65	−1·60
7	−68	−1·68
8	−71	−1·75

workers[17] and spectroscopically by us[14]. This means that the process would involve opening of cyclic skeleton of $(HNPO_2)_3^{3-}$ anion, however without being observed experimentally, to yield first diimido-cyclo-triphosphate. This was identified correctly by Narath, Lohman and Quimby[9] who also proved that the substance has not the structure of chain-like diimidodiphosphate, as suggested erroneously by de Ficquelmont[7].

Also in aqueous alkaline solutions (pH 11 and 13) amidochloro-cyclo-triphosphazenes $N_3P_3Cl_4(NH_2)_2$ and $N_3P_3Cl_5(NH_2)$ undergo hydrolysis to form cyclo-triphosphazane. This compound is very stable against hydrolysis in this medium and only in strogly alkaline solutions and at higher temperatures it hydrolyses with ring opening of the anionskeleton by the mechanism proposed by us in previous work[18].

If amido-chloro-cyclo-triphosphazenes $N_3P_3Cl_4(NH_2)_2$ and $N_2P_3Cl_5(NH_2)$ are suspended in aqueous NaOH solution of concentration higher than 1 mol/l, due to fast reaction, there proceeds local overheating the reaction mixture and formation of diimidotriphosphate, diphosphate, phosphate and other compounds that can be considered to be the products of the hydrolysis of primary formed cyclo-triphosphazane that cannot be detected under these conditions.

Summarizing, our results show that the presence of one or two amido groups on one phosphorus atom in amidochloro-cyclo-triphosphazenes does not lead, by contrast to $[NP(NH_2)_2]_3$, in aqueous solutions initially to the opening of cyclic skeleton of these compounds but it results in formation of cyclo-triphosphazane anions after hydrolytic cleavage of chlorine atoms and amido groups.

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Translated by J. Hetflejš.