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STUDIES OF NITROGEN-PHOSPHORUS COMPOUNDS. XXVII[1)]
THE HYDROLYSIS OF TETRAMERIC PHOSPHORUS NITRIDE DIAMIDE

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When an aqueous solution of $N_4P_4(NH_2)_8$ was refluxed at 100°C, the compound was initially hydrolyzed to $PO(NH_2)_3$ and $P_2O_2NH(NH_2)_4$, and they were converted into $PO(ONa)(NH_2)_2$. The rate of hydrolysis was remarkably slow at room temperature, however, the composition of the hydrolysis products was similar to that at 100°C. In a sosium hydroxide solution, $N_4P_4(NH_2)_8$ was converted directly into $PO(ONa)(NH_2)_2$ at an elevated temperature. An acid-hydrolysis behavior was resembled that in the neutral-hydrolysis, but the reaction was accelerated with an acid strength. The formation of tetrametaphosphimate by the hydrolysis of $N_4P_4(NH_2)_8$, that had been hitherto claimed, could not be recognized in this study.

The amidated derivatives of the lower polymers of phosphorus nitride dichloride have an interest as the fireproof material[2,3)] and fertilizer.[4,5)] The present author had previously reported the synthesis of $N_3P_3(NH_2)_6$[6)] and the formation of $PO(ONa)(NH_2)_2$ by the alkali-hydrolysis of the trimeric variety.[7)] In this work, the hydrolysis of $N_4P_4(NH_2)_8$ in the neutral, alkali and acid solutions was investigated. The experimental results were partially different from the previous explanations.[8,9)] And so the hydrolysis behavior of $N_4P_4(NH_2)_8$ will be described as compared with that of $(NPCl_2)_4$.

$(NPCl_2)_4$ (mp. 123.0-123.7°C) used as the raw material was obtained by the fractional sublimation under a vacuum from $(NPCl_2)_n$ (n=3-7) which was synthesized by the reaction between phosphorus pentachloride and ammonium chloride. After $(NPCl_2)_4$ was fully treated with liquid ammonia in the presence of a little amount of dioxane. The resulting product was dissolved in water, and the addition of ethanol into the solution gave rise to the precipitate of $N_4P_4(NH_2)_8 \cdot H_2O$, which was separated from the mother liquor, fianlly vacuum-dried, and used for the hydrolysis examinations.

The elution chromatograms of a mixture of the standard materials and some hydrolysis products are shown in Fig. 1.

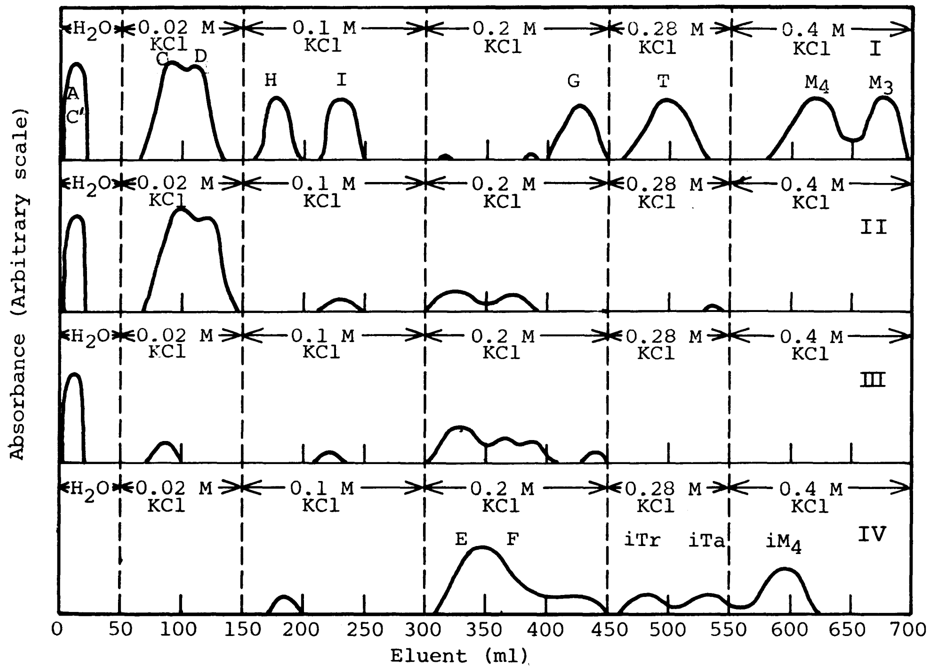

Fig.1 Chromatographic analysis of hydrolysis products of $N_4P_4(NH_2)_8$ and $(NPCl_2)_4$ at room temperature.

I: Mixture of standard materials [A: $N_4P_4(NH_2)_8$, C: $P_2O_2(NH)(NH_2)_4$, C': $PO(NH_2)_3$, D: $PO(ONa)(NH_2)_2$, H: $PO(ONa)_2NH_2$, I: Na_2HPO_4, G: $Na_4P_2O_7$, T: $Na_5P_3O_{10}$, M_3: $(NaPO_3)_3$, M_4: $(NaPO_3)_4$]

II: Hydrolysis product of $N_4P_4(NH_2)_8$ for 20 day

III: Hydrolysis product of $(NPCl_2)_4$ in ether-aqueous ammonia solution for 1 hr

IV: Hydrolysis product of $(NPCl_2)_4$ in ether-water solution for 2 hr
Estimated components [E: $P_2O_2(NH)(NH_2)_2(OH)_2$, F: $P_2O_2(NH)(OH)_4$, iTr: $P_3O_3(NH)_2(OH)_5$, iTa: $P_4O_4(NH)_3(OH)_6$, iM_4: $P_4N_4O_4H_4(OH)_4$]

The neutral-hydrolysis of $N_4P_4(NH_2)_8$ were examined at the room and elevated temperatures, and the hydrolysis products were analyzed by means of the ion-exchange chromatography. When a solution of 0.05 M $N_4P_4(NH_2)_8$ was refluxed at 100°C, the compound was initially hydrolyzed into $PO(NH_2)_3$ and $P_2O_2NH(NH_2)_4$. Further, they converted to $PO(ONH_4)(NH_2)_2$ as a main product in this case, and a part of the diamidophosphate gradually decomposed to monamidophosphate. In an aqueous solution, $N_4P_4(NH_2)_8$ was stable for about 3 days at room temperature, after that was gradually hydrolyzed. Chromatogram II shows an elution curve for the hydrolysis product of $N_4P_4(NH_2)_8$ after 20 days. The rate of hydrolysis was remarkably slow, the composition of the hydrolysis products was similar to that at 100°C. Chromatogram III shows the elution for the hydrolysis product of $(NPCl_2)_4$ (0.5 g) in an ether (7.5 ml)-aqueous ammonia (3 M, 8 ml) solution. $(NPCl_2)_4$ was partly converted into $N_4P_4(NH_2)_8$ in spite of the presence of water. The other products were some phosphoryl triamide, tetramidoimidodiphosphate, orthophosphate and imidodiphosphate. $(NPCl_2)_4$ (0.5 g) was also hydrolyzed in an ether (15 ml)-water (5 ml) solution. The product was neutralized by employing aqueous ammonia, and analyzed by means of the ion-exchange chromatography. The result is shown as chromatogram IV. In this hydrolysis, $(NPCl_2)_4$ converted into a cyclic tetrametaphosphimate, simultaneously, it was gradually hydrolyzed into imidotetraphosphate, imidotriphosphate, imidodiphosphate, and some amidophosphate.

Moureu etc.[8] had observed by a microscopic examination that the hydrolysis product of $N_4P_4(NH_2)_8$ resembled closely to $P_4N_4O_4H_4(ONH_4)_4 \cdot 4H_2O$ which[10] was obtained by the hydrolysis of $(NPCl_2)_4$. And then it was concluded that the hydrolysis product of $N_4P_4(NH_2)_8$ was the same compound to $P_4N_4O_6H_6(ONH_4)_2$. However, the components had not been examined by other analytical technics. Their result was refered in a science book.[11] To ascertain whether their result is true, present author have also investigated the hydrolysis behaviors of $(NPCl_2)_4$ and $N_4P_4(NH_2)_8$. As the above-mentioned results, the cyclic tetrametaphosphimate was obviously formed by the hydrolysis of $(NPCl_2)_4$, but, the formation of tetrametaphosphimate by the hydrolysis of $N_4P_4(NH_2)_8$ could not be recognized in this work.

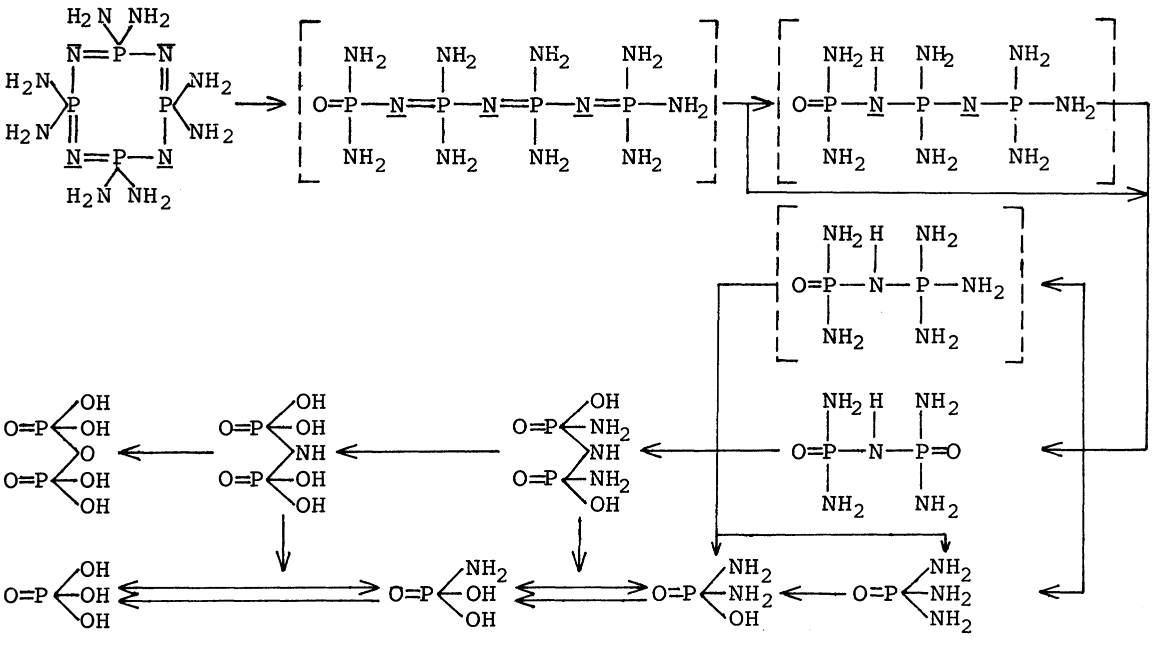

Fig.2 Hydrolysis of $N_4P_4(NH_2)_8$ in neutral or acid solution.

On the alkali-hydrolysis, in a sodium hydroxide solution $N_4P_4(NH_2)_8$ was converted directly into $PO(ONa)(NH_2)_2$ without any intermediate products by refluxing for 3 hr at about 100°C. The rate of the alkaline-hydrolysis obeyed that of a first-order equation, the rate constants being 1.0×10^{-3}, 2.5×10^{-3}, 1.9×10^{-2} and 4.2×10^{-2} at 50, 60, 80 and 90°C, respectively. These values were about 2.7 times that of the alkali-hydrolysis of $N_3P_3(NH_2)_6$, and the activation energy of the reaction was 20.8 Kcal/mol.

It was observed by the examinations that the acid-hydrolysis behavior was resembled that in the neutral-hydrolysis. A process of the neutral and acid-hydrolysis is shown in Fig. 2. The reaction was accelerated with an acid strength, the existences of $PO(NH_2)_3$ and $P_2O_2NH(NH_2)_4$ which were unstable in an acid solution could not be recognized. In this case, $N_4P_4(NH_2)_8$ was hydrolyzed up to the formation of ortho-phosphates and diphosphates.

Reference

1) Part XXVI of this series: E.Kobayashi and S.Kamagami, Nippon Kagaku Kaishi, 1975, 2098.
2) C.A.Redfarm and H.Coates (Albright & Wilson Ltd.), Brit., 788,785 (1958).
3) Erik R.Nielsen and William L.Stepp, U.S., 3,348,926 (1967).
4) T.Z.Wakefield, E.S.Allen, F.J.McCullough, C.R.Sheridan, and J.J.Kohlen, J. Agr. Food Chem., 19, 99 (1971).
5) W.Wanek, L.Ondracek, and J.Hampl, Z. Pflanzenernaehr. Bodenk., 128, (3), 169 (1971); Agrochimia, 11, (6), 177 (1971).
6) E.Kobayashi, Nippon Kagaku Kaishi, 1972, 38; Journal of The National Chemical Laboratory for Industry, 68, 19 (1973).
7) E.Kobayashi, Nippon Kagaku Kaishi, 1973, 1437; Journal of The National Chemical Laboratory for Industry, 69, 470 (1974).
8) H.Moureu and P.Rocquet, Bull. Soc. Chim., [V] 829 (1936).
9) K.Dostal, M.Kouril, and J.Novak, Z. Chem., 4 (9), (1964); Chem. Abstr., 62, 4670 (1965).
10) H.N.Stokes, Amer. Chem. Journal, 18, 780 (1896).
11) Charles B.Colburn, "Developments in Inorganic Nitrogen Chemistry I" Elsevier, Amsterdam (1966), p356.

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