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The Reaction of *cyclo*-Triphosphate with Ethylenediamine

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The reaction of sodium *cyclo*-triphosphate (P_{3m}) with ethylenediamine (en) was studied with special attention paid to the kinds and amounts of products under various conditions and to its reaction mechanism. 1) The reaction of P_{3m} with ethylenediamine in the pH range of 8—12 gave six new compounds; three of them were identified as *N*,*N*-bis(2-aminoethyl)phosphorodiamidate (P_1-en$_2$), *N*-(2-aminoethyl)amidodiphosphate (P_2-en), and *N*-(2-aminoethyl)-*P*-amidotriphosphate (P_3-en). 2) The formation of P_3-en and P_2-en was most favored at a pH near 10(about 32 and 9% respectively), while that of P_1-en$_2$ proceeded extensively at pH 10—12(about 12%). 3) The amounts of products varied greatly depending on the mixing ratio of P_{3m} and ethylenediamine. P_1-en$_2$ was the predominant product at en/$P_{3m}>1$, while P_3-en was at en/$P_{3m}\leqq 1$. 4) At a pH value below 10, tetra-(P_4) and pentaphosphate (P_5) were formed in addition to the above products. The reaction between P_{3m} and ethylenediamine scarcely proceeded under acidic conditions. 5) Ortho-(P_1), pyro-(P_2), and triphosphate (P_3) did not react with ethylenediamine at all. 6) The reaction mechanism between P_{3m} and ethylenediamine was discussed.

Linear condensed phosphates have found wide practical applications as food and drug additives, detergents, and fertilizers,[1–3] but little is known about the applications of cyclic condensed phosphates.[4] It was first reported by Quimby and Flautt[5] in 1959 that cyclotriphosphate (P_{3m}), a six-membered cyclic phosphate, readily undergoes a ring-opening reaction in the presence of ammonia to give amidotriphosphate. After that, it was reported that P_{3m} reacts with amines, such as alkylamine,[6,7] 1,6-hexandiamine[8] and amino acids,[9–12] to yield new compounds with a P–N bond in their molecules. Recently, it was found that P_{3m} also reacts with other organic compounds, such as alcohols,[13] sugar,[13] and nucleoside,[14–19] and that it is effective for the stabilization of vitamin C.[20] As a result, extensive attention has been paid to the potential commercial applications of P_{3m}. However, the details of the reaction of P_{3m} with these organic compounds still remain unclear. In the present study, therefore, P_{3m} was allowed to react with ethylenediamine, the simplest member of the diamine family, under various conditions, and the kinds and amounts of the products as well as the reaction mechanism were investigated by using anion-exchange chromatography, chemical analysis for phosphorus and ethylenediamine, and IR spectroscopy.

Experimental

Chemicals. The sodium *cyclo*-triphosphate, $Na_3P_3O_9\cdot 6H_2O$, was prepared by the procedure described in a previous paper[21] and recrystallized five times from an aqueous solution. Unless otherwise stated, guaranteed reagents from Wako Chemical Industries, Ltd., were used without further purification.

Reaction between cyclo-*Triphosphate and Ethylenediamine.* A 0.5 mol dm^{-3} portion of the sodium *cyclo*-triphosphate (P_{3m}) solution was mixed with a 0.5 or 5 mol dm^{-3} ethylenediamine (en) solution (molar ratio; P_{3m}:en=1:1 and 1:10), the mixed solution was controlled to the prescribed pH by adding a 6 mol dm^{-3} hydrochloric acid or sodium hydroxide solution(pH:12, 10, and uncontrolled), and the reaction was allowed to proceed at room temperature. Since the pH of the mixed solutions lowered as the reaction progresses, it was held at the prescribed pH, when required, by adding a sodium hydroxide solution.

Anion-exchange chromatography, the determination of phosphorus, and IR spectroscopy were carried out by the methods described in a previous paper.[21]

A Yanagimoto Micro Elemental Analyzer, MT-2 type, was used for the determination of ethylenediamine in the reaction products.

Results and Discussion

Reaction of cyclo-*Triphosphate with Ethylenediamine.* The initial pH of the mixed solution of P_{3m} and ethylenediamine at a molar ratio of 1:1 was above 14, but it was lowered sharply with the progress of the reaction, reaching about 12 after 2 h and going down to about 8.7 after 3 d. This indicates that P_{3m} reacted with water or ethylenediamine to afford chain-phosphates or their derivatives. To prove this, we attempted to separate and determine the reaction products by means of anion-exchange chromatography. An example of the results obtained is given in Fig. 1, which shows the elution patterns for the reaction products after 1 and 7 d. Then, the pH values of the solution were about 9.2 and 8.3 respectively. As can be seen, elution peaks of P_1, P_2, and P_3 appeared after 1 d. In addition, a large peak of an unknown compound(designated as Compound D) was observed between the peaks of P_1 and P_2, and two other peaks of unknown compounds(Compounds A and B) were noticed before the peak of P_1. Furthermore, peaks of tetra-(P_4) and pentaphosphate(P_5) were also observed after 39 d, though they are not shown in Fig. 1.

Figure 2 shows the changes in the amounts of P_1, P_2, P_3, P_4, and P_5, as well as in Compounds A, B, and

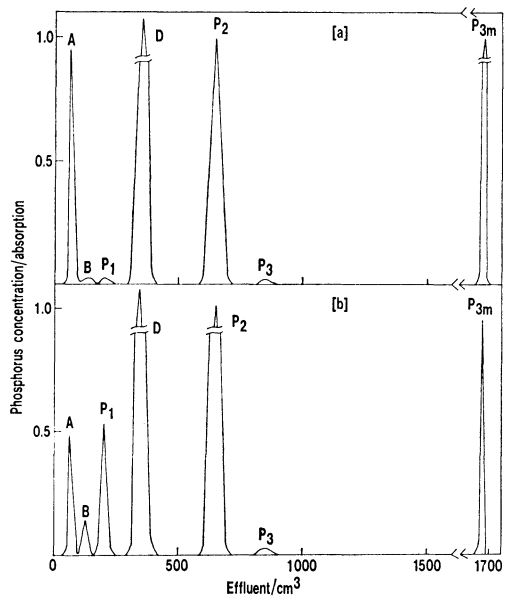


Fig. 1. Elution patterns for the reaction products of P_{3m} with ethylenediamine.
[a]: After 1 d(pH 9.2), [b]: after 7 d(pH 8.3).

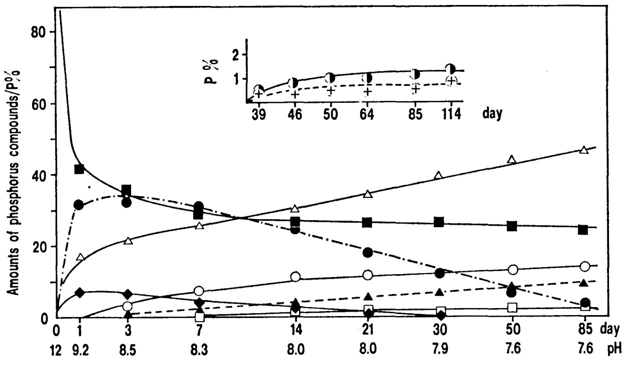


Fig. 2. Change of the amounts of phosphorus compounds in the reaction of P_{3m} with ethylenediamine.
—○—: P_1, —△—: P_2, —□—: P_3, --⊕--: P_4, —◑—: P_5, —◆—: Compound A, --▲--: B, —·—●—·—: D, —■—: P_{3m}.

D, with the passage of time or with the decrease in the pH. It is apparent from the figure that Compound D began to be formed immediately after the reaction, and that its amount reached a maximum level of 32.4% after 3 d, followed by a gradual decrease with the reaction time or with a decrease in the pH. A similar tendency was observed in Compound A. Compound B, on the other hand, was first observed after 3 d, and its amount increased with the time, reaching about 8.7% after 114 d. The amounts of P_1 and P_2 also showed a gradual increase with the time, reaching about 13.8 and 48.2% respectively after 114 d. The formation of P_2 was particularly marked. These results indicate that the formation of Compounds A and D is favored by a high pH. To provide further evidence for this, the reaction of P_{3m} with ethylenediamine was carried out at the controlled pH values of 12 and 10 at a mixing ratio of 1:1.

Figure 3 shows the elution patterns for the reaction

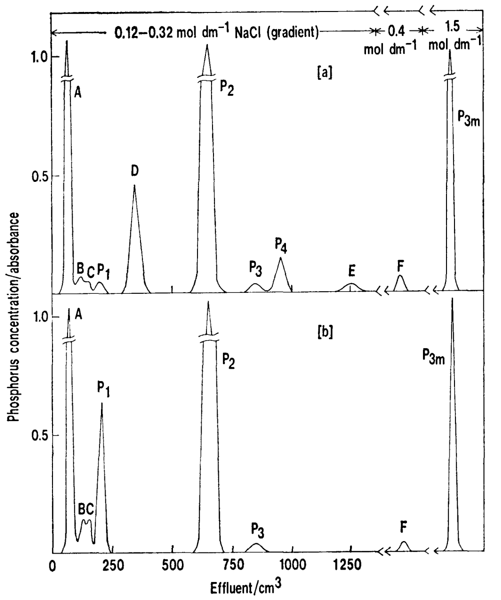


Fig. 3. Elution patterns for the reaction products of P_{3m} with ethylenediamine at pH 12.
[a]: After 1 d, [b]: 17 d.

mixture after 1 and 17 d at pH 12. In this experiment, the gradient elution technique with a 0.12—0.32 mol dm^{-3} sodium chloride solution was used for the eluant up to 1600 cm^3, while the step-wise elution method with 0.4 and 1.5 mol dm^{-3} sodium chloride solutions was used for the elution of an unknown compound F and P_{3m}, respectively. Compared with the reaction of P_{3m} with ethylenediamine at an uncontrolled pH, we observed remarkable differences in the kinds and amounts of products at pH 12. That is, a small peak of an unknown compound(Compound C) was observed between the elution peaks of P_1 and Compound B. In addition, a peak of an unknown compound(Compound E) was also found at an eluant of 1250 cm^3, and another one of an unknown compound (Compound F) when the mixture was eluted with a 0.4 mol dm^{-3} sodium chloride solution. In short, six unknown compounds(Compounds A, B, C, D, E, and F) were formed by the reaction of P_{3m} with ethylenediamine at pH 12. Sodium pyrophosphate decahydrate, $Na_4P_2O_7 \cdot 10H_2O$, began to precipitate after 3 d, and its amount increased with the time. P_4 was formed in significant quantities(about 9.8%) in the initial stage of the reaction(up to 5 d), but its amount decreased after that with the lapse of time. Figure 4 shows the changes in the amounts of P_1, P_2, P_3, and P_4, as well as in Compounds A through F, with the time. As can be seen from Fig. 3, the elution peaks of Compounds B and C were too close together to be determined. Also, all attempts to separate Compounds B and C by changing the elution conditions failed. The sum of the amounts of Compounds B and C is, therefore, shown in Fig. 4. A comparison of Fig. 4 with Fig. 2 indicates a marked difference between the reactions carried out at pH 12 and those carried out with no control of the pH. Particularly, when the pH of the solution was not controlled, the formation of Compound D was apparently favored under mildly

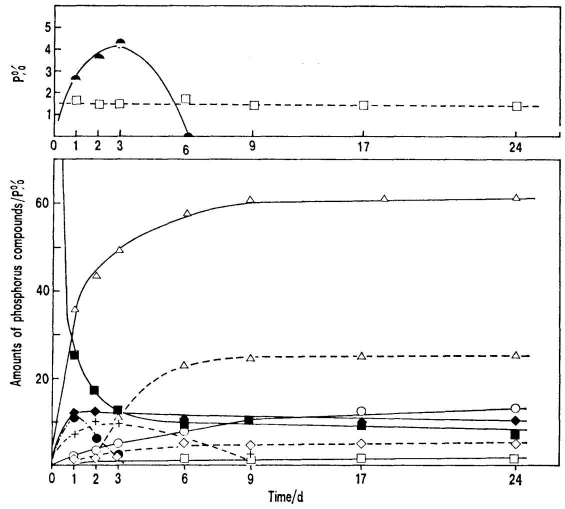


Fig. 4. Change of the amounts of phosphorus compounds in the reaction of P_{3m} with ethylenediamine at pH 12.
—○—: P_1, —△—: P_2(total), --△--: P_2(precipitated) —□—: P_3, --⊕--: P_4, —◆—: A, --◇--: B+C, —·—●—·—: D, —◓—: E, --□--: F, —■—: P_{3m}.

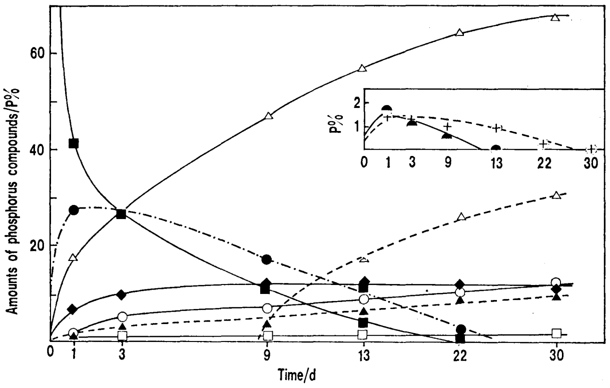


Fig. 5. Change of the amounts of phosphorus compounds in the reaction of P_{3m} with ethylenediamine at pH 10.
—○—: P_1, —△—: P_2(total), --△--: P_2(precipitated) —□—: P_3, --⊕--: P_4, —◆—: A, —▲—: B, —·—●—·—: D, —◓—: E, —■—: P_{3m}.

alkaline conditions(pH 10—8.5). Compound A, on the contrary, was produced more readily in highly alkaline regions(pH 12). Compounds C, E, and F were also formed in high pH regions, but their amounts were rather small. Compound E was produced in significant quantities in the initial stage of the reaction (up to 3 d), but disappeared completely after 6 d. In addition, the precipitation of $Na_4P_2O_7 \cdot 10H_2O$ was observed after 3 d at pH 12. The same phenomenon has been experienced by the present authors in the reaction of P_{3m} with L-valine[21] or glycine.[22]

In contrast, the products obtained by the reaction of P_{3m} with ethylenediamine at pH 10 were very similar to those in the reaction at an uncontrolled pH; the products obtained at pH 10 were Compounds A, B, D, and E, but Compounds C and F were not formed at all. The only difference between the two reactions was that Compound E was produced at pH 10, while P_5 was produced at an uncontrolled pH.

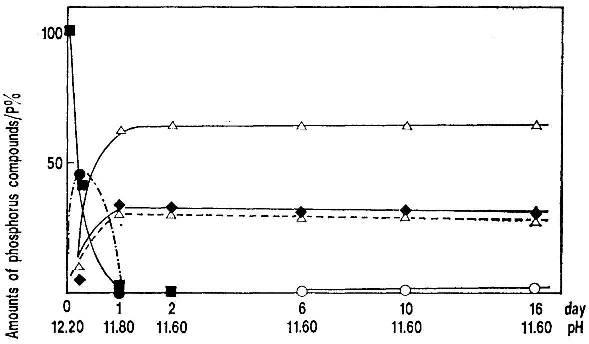


Fig. 6. Change of the amounts of phosphorus compounds in the reaction of P_{3m} with ethylenediamine.
—○—: P_1, —△—: P_2(total), --△--: P_2(precipitated) —◆—: A, —·—●—·—: D —■—: P_{3m}.

Figure 5 shows the changes in the amounts of products (Compounds A, B, D, and E), as well as P_1, P_2, P_3, P_4, and P_{3m}, with the lapse of time at pH 10. It is apparent from Fig. 5 that Compound D was formed in considerable quantities in the initial stage, its amount reaching a maximum level of about 28.6% after 1 d and then decreasing with time. The amount of Compound A, on the other hand, gradually increased for the first week and after that was almost constant(about 11.5%).

Figures 2, 4, and 5 show that Compound A is stable at a pH of 10 or higher. The amounts of P_4 and Compound E were very small, about 1.5% for both.

The formation of the products(Compounds A, B, C, D, E, and F) in the reaction between P_{3m} and ethylenediamine at a molar ratio of 1:1 under various pH conditions may be summarized as follows: 1) Compound D was rapidly formed in the initial stage of the reaction(1—3 d) at pH 10—8.5, its amount reaching about 32%. 2) Compound A was formed in significant quantities at pH 10—12, its amount reaching about 12%. This compound was stable within this pH region for a long time(30 d). 3) Compound B was formed at pH 10 over a long period(30 d), its amount reaching about 9.2%. However, it was found only in minute quantities at pH 12, and the rate of its formation was also very low at a pH of 8.5 or lower. 4) Compound C was produced only in a high pH region(12 or higher) and in small quantities(about 2%). 5) Compound E was formed in the initial stage of the reaction (1—3 d) at a pH of 10 or higher, but it was decomposed almost completely after two weeks. Its amount was about 4.5% at pH 12. 6) Compound F was formed at a pH of 12 or higher, but its amount was as small as about 1.7%. Besides these compounds, the formation of P_4 and P_5 was also observed at a pH of 10 or lower; their amounts tended to increase slightly as the pH was lowered to near neutral. The mechanism of the formation of P_4 and P_5 will be presented in detail later.

No reaction of P_{3m} with ethylenediamine took place under acidic conditions. This is probably ascribable to the formation of inactive $H_3N^+CH_2CH_2NH_2$ or $H_3N^+CH_2CH_2N^+H_3$.

Next, the effect of the mixing ratio of P_{3m} and ethyl-

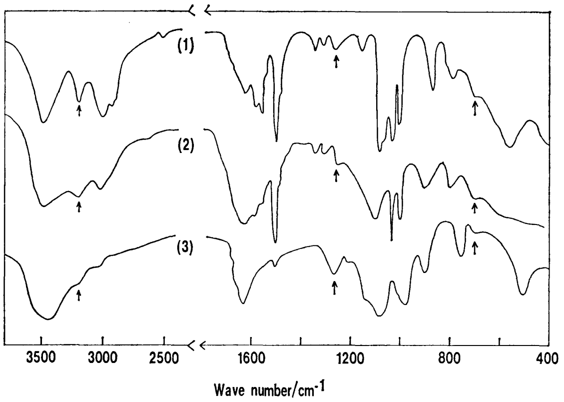


Fig. 7. IR spectra of the compounds A, B, and D. (1): Compound A, (2): B, (3): D. Arrow(↑): absorption due to the P–N bond.

enediamine on the kinds and amounts of reaction products was studied. Figure 6 shows the changes in the amounts of various phosphates with the time at a molar ratio of P_{3m}:en=1:10. As can be seen, the reaction proceeded at a higher rate in the presence of a large excess of ethylenediamine. The products obtained in the reaction were P_1, P_2, P_3, and Compounds A, D, and E. However, the date for P_3 and Compound E are omitted in Fig. 6, because their amounts are very small. In response to the consumption of P_{3m}, Compound D began to be formed immediately after the reaction, its amount reaching about 47% after 5 h; thereafter, it decreased rapidly. On the contrary, Compound A began to be formed after 5 h, its amount reaching about 37% after 1 d. P_2 was also formed concurrently with the formation of Compound A, its amount reaching about 64%. Precipitates of $Na_4P_2O_7 \cdot 10H_2O$ were observed about 3 h after the reaction. As may be apparent from Fig. 6, the reaction of P_{3m} with ethylenediamine at a molar ratio of 1:10 afforded Compound A and P_2 as the main products; the amount of the former(about 32% as phosphorus concentration) is just half that of the latter (about 64%). This suggests that Compound A is an orthophosphate derivative of ethylenediamine.

The results obtained by the reactions in the mixing-ratio range from P_{3m}:en=1:0.1 to 1:10 may be summarized as follows: the formation of Compound A was predominant at P_{3m}/en<1, and that of Compound D, at P_{3m}/en≧1.

Molecular Structures of the Three Unknown Compounds, A, B, and D. Compounds A, B, and D were isolated by anion-exchange chromatography according to the method described in the previous paper;[21] the structure of each compound was then investigated by means of chemical analysis for phosphorus and ethylenediamine and by means of IR spectroscopy, as well as by means of its structural change with the pH.

Chemical analysis revealed that the P/en ratios are 1:2, 2:1, and 3:1 for Compounds A, B, and D respectively. This indicates that Compound A may be a P_1-derivative of ethylenediamine containing P_1 and ethylenediamine in the molar ratio of 1:2, Compound B, a P_2-derivative of ethylenediamine(P_2:en=1:1), and Compound D, a P_3-derivative of ethylenediamine(P_3:en=1:1).

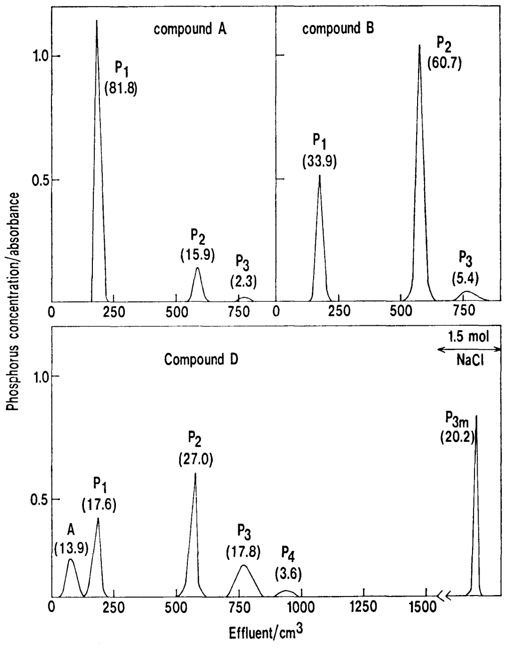


Fig. 8. Decomposition of the compounds A, B, and D at pH 3.

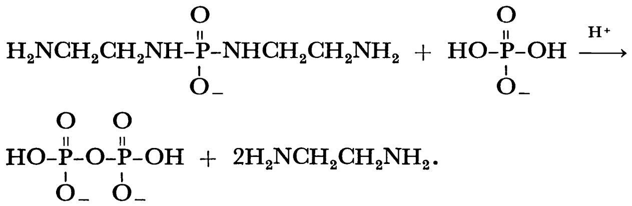
Figure 7 shows the IR spectra of Compounds A, B, and D as measured by means of a KBr tablet. For Compound A, characteristic absorptions due to the P–N bond were observed at about 3330—3150, 1270, 875, and 700 cm^{-1},[23–25] while those attributable to the P–O bond were noticed at about 1160 and 970—1050 cm^{-1}.[26,27] Absorptions that can be assigned to the $-CH_2-$ group were also observed at 2925, 2850, and 1470 cm^{-1},[28] while characteristic absorptions due to the $-NH_2$ were present at about 3500 and 1065 cm^{-1}.[28] For Compound B, absorptions ascribable to the P–N bond were noticed at about 3330—3150, 1260, and 700 cm^{-1}, but the absorption due to the P–N bond near 875 cm^{-1} was uncertain because of overlapping with the strong absorption due to the P–O–P bond near 900 cm^{-1}. A peak that can be assigned to the P–O bond was also observed at 970—1050 cm^{-1}.

Compound D, as in the case of Compound B, showed characteristic absorptions due to the P–N, P–O–P, and P–O bonds. Also, there were characteristic bands[29] of the vibrations of the triphosphate anion at about 1230(ν_{as} PO_2), 1160(ν_{as} PO_3), 1000(ν_s PO_3), 735($\delta_s PO_2$), and 510 cm^{-1} in Compound D.

These results of chemical analysis and IR spectroscopy indicate that Compounds A, B, and D are phosphate derivatives of ethylenediamine containing the P–N bond in their molecules. Compounds B and D, which showed absorption due to both the P–N and P–O–P bonds, can be considered as pyro- and triphosphates derivatives of ethylenediamine. Compound A, on the other hand, has no P–O–P bond in the molecule, and so it may be regarded as an orthophosphate derivative of ethylenediamine.

To provide further evidence for the above, Compounds A, B, and D were dissolved in distilled water, allowed to stand for 15 min. at a pH controlled to 3 by adding dilute hydrochloric acid, and then analyzed by anion-exchange chromatography. The results are shown in Fig. 8, the numerals in which are the amounts of products represented in P%. It is apparent from Fig. 8 that Compound A, upon acidification (to pH 3), was decomposed to give P_1 in about an 80% yield. P_2 and P_3 were also formed at the same time, though in small amounts. This clearly indicates that Compound A is a P_1-derivative of ethylenediamine(P_1-en_2), in which two molecules of ethylenediamine are combined with P_1. On the other hand, Quimby⁵⁾ and also Feldmann and Thilo⁶⁾ reported that, when amidophosphates having the P–N bond were acidified, the condensation of phosphate took place and amidotriphosphate was recyclized to P_{3m}.

The formation of P_2 and P_3 by the hydrolysis of P_1-en_2 under the acidic conditions in the present study may be explained by the mechanism described by Quimby⁵⁾ and by Feldmann and Thilo:⁶⁾



$$H_2NCH_2CH_2NH\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}\text{-}NHCH_2CH_2NH_2 + HO\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}\text{-}OH \xrightarrow{H^+} HO\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}\text{-}O\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}\text{-}OH + 2H_2NCH_2CH_2NH_2.$$

That is, the P_1 formed by the hydrolysis of P_1-en_2 reacts with undecomposed P_1-en_2 or partially hydrolyzed $H_2NCH_2CH_2NH\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}\text{-}OH$ (P_1-en) to form P_2, which in turn reacts with P_1-en_2 or P_1-en to give P_3.

Compound B, when acidified, affords about 61% in P_2, 34% in P_1, and 5% in P_3. This indicates that this compound is $^-O\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}\text{-}O\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}\text{-}NHCH_2CH_2NH_2$ (P_2-en), in which one molecule of ethylenediamine is attached to P_2. The large amount of P_1 observed may be ascribed to the hydrolysis of the P_2 once formed.

It is apparent from Fig. 8 that, under acidic conditions, Compound D is changed into P_1, P_2, P_3, P_4, and Compound A, and that about 20% of it is recyclized to P_{3m}. This shows clearly that Compound D is a triphosphate derivative of ethylenediamine.

It was demonstrated that Compound A is *N,N′*-bis(2-aminoethyl)phosphorodiamidate $H_2NCH_2CH_2NH\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}\text{-}NHCH_2CH_2NH_2$, Compound B, *N*-(2-aminoethyl)amidodiphosphate $^-O\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}\text{-}O\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}\text{-}NHCH_2CH_2NH_2$, and Compound D, *N*-(2-aminoethyl)-*P*-amidotriphosphate $^-O\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}\text{-}O\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}\text{-}O\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O_-}{|}}{P}}\text{-}NHCH_2CH_2NH_2$, from the results of the chemical analysis for phosphorus and ethylenediamine and from the results of IR spectroscopy, as well as from the results of the hydrolysis of these compounds under acidic conditions.

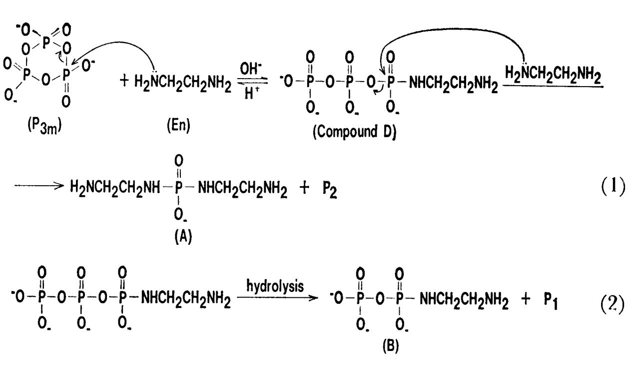


Fig. 9. Mechanism of the reaction of P_{3m} with en.

The structures of Compounds C, E, and F have not yet been characterized because they were formed in only minute amounts and could not be isolated in a pure form.

Reaction of Short-chain Phosphates with Ethylenediamine. A solution of trisodium orthophosphate (P_1), tetrasodium pyrophosphate (P_2), or pentasodium triphosphate (P_3) was mixed with an ethylenediamine solution in a molar ratio of 1:1, and then the mixed solution was adjusted with a hydrochloric acid or sodium hydroxide solution to pH 12 and allowed to react at room temperature. No reaction products were observed at all in the reaction of ethylenediamine with P_1, P_2, or P_3.

Reaction Mechanism of P_{3m} and Ethylenediamine. The mechanism of the reaction between P_{3m} and ethylenediamine at pH 10—12 is summarized in Fig. 9. Probably, the first step of the reaction is the nucleophilic attack of the lone pair of the nitrogen atom in ethylenediamine on the phosphorus atom in P_{3m} to cause a ring opening of *cyclo*-triphosphate, forming P_3-en. The P_3-en once formed is then attacked by free ethylenediamine or undergoes hydrolysis to give P_1-en_2 or P_2-en.

This reaction mechanism can reasonably explain the fact that P_3-en, formed predominantly in the initial stage of the reaction at pH 10—12, was gradually converted into P_1-en_2, P_2-en, and other phosphates with the passage of time. In the presence of a large excess of ethylenediamine(P_{3m}:en=1:5—1:10), it was found that P_3-en, which was formed in large quantities immediately after the reaction, completely disappeared after 1 d, leaving only P_1-en_2 and P_2. This fact also supports the above mechanism in which the reaction of P_3-en with free ethylenediamine affords P_1-en_2.

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