The Formation of Higher Linear Phosphates during Degradation Reactions of Di-, Tri- and Tetraphosphates in the Presence of Aluminum(III) Ion

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Linear phosphates which contain one more P atom in their molecules than the parent phosphates were found in the degradation products of the parent di-, tri- and tetraphosphate under the presence of aluminum(III) ions. These side reactions occurred only during the cleavage reactions of the linear polyphosphates.

We have investigated the cleavage reactions of the P-O-P linkages of cyclo-phosphates and linear phosphate oligomers under various conditions. The hydrolysis rates of these oligomers are increased most strongly by H^+ ions[1,2] and also increased by various cations[3,4] which form complexes or ion-pairs with these phosphate anions. In alkaline solutions, the rates are affected not only by the concentration of the OH^- ion but also by the counter ions of the hydroxide ion.[5,6] In this study, the degradation reactions of di- and triphosphates, which are the important constituents of ADP and ATP, were investigated under several conditions, and trimer and tetramer were found in the degradation products of the di- and triphosphates, respectively. A " monophosphate radical" which is formed by the cleavage of P-O-P bonds in di- and triphosphates sometimes attacks end P atoms in di- or triphosphate which remained unhydrolyzed and were attracted to the aluminum(Ⅲ) ion; therefore tri- and tetraphosphates are formed. These "condensation" reactions occurred only when the P-O-P bridges of the phosphates were cleaved. In the same manner, pentaphosphate was also found in the degradation products of tetraphosphate in the presence of Al^{3+} ions. Except in weakly acidic solutions, tetraphosphate is hydrolyzed by end-group clipping, thus forming monophosphate which as a free radical may attack the tetraphosphate and recombine with each other. Usually the condensed phosphates have been prepared by the thermal decomposition of a solid hydrogen monophosphate. Our result suggests that these condensed phosphates can be prepared in dilute aqueous solutions of the lower condensed phosphates. The experimental details of the preparation of the condensed phosphates used in this study are presented in our earlier papers.[4,7] The degradation samples were analyzed using the liquid chromatographic system described previously.[8] The concentration of the diphosphate to be hydrolyzed was fixed as 2.5×10^{-4} mol dm^{-3} in the test solutions, to which an equimolar Al^{3+} ion was added and the pH of the solutions were adjusted at pH 3. The test solutions were hydrolyzed at various temperatures and the hydrolysis samples were analyzed by the liquid chromatographic system. In the hydrolysis samples of diphosphate, triphosphate was found as shown in Figure 1(a). The formation of triphosphate was eminent when diphosphate was hydrolyzed at 70 ℃. The distribution of di-, mono- and triphosphate during the hydrolysis of diphosphate under the presence of equimolar Al^{3+} at 70 ℃ is shown in Table 1.

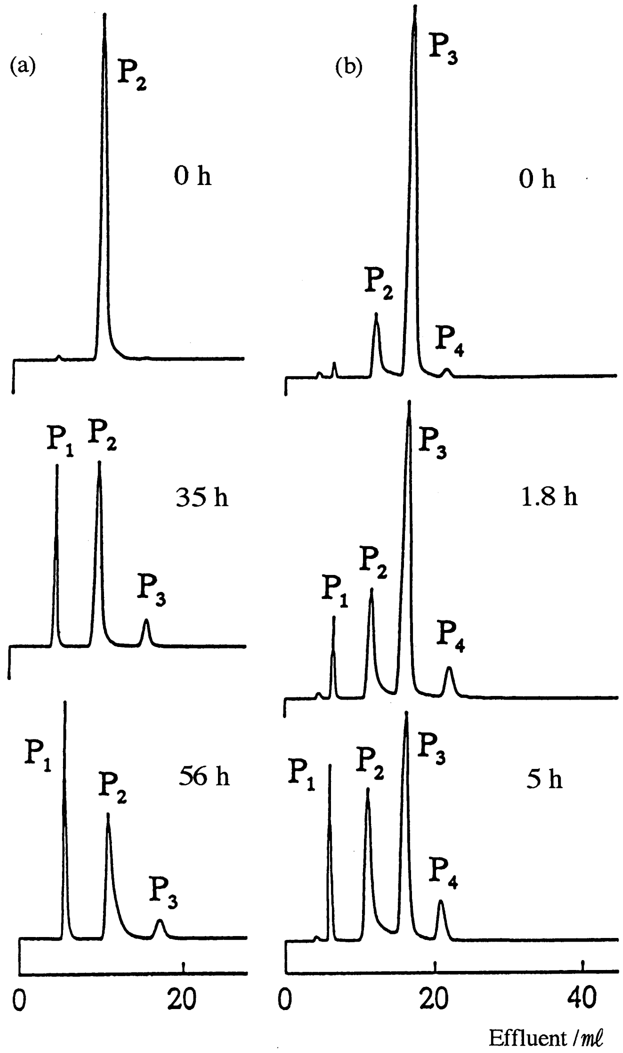

Figure 1. Chromatograms of the degradation products ; (a) diphosphate (b) triphosphate .

Maximum yield of tetraphosphate was 9.5%(as P) at 70 ℃ when 2.5×10^{-3} mol dm^{-3} of triphosphate was hydrolyzed under the presence of equimolar Al^{3+}. The chromatograms of the hydrolysis samples of triphosphate are shown in Figure 1(b) and

Table 1. The concentration(P%) of each phosphate at various times in the degradation products of di-, tri- and tetraphosphate

	Time/h	P_1	P_2	P_3	P_4	P_5	P_{3m}[a]
P_2	0	0.8	98.6	0.6			
	7	7.1	88.2	4.4			
	14	12.5	80.8	6.5			
	21	17.8	74.2	7.9			
	28	22.4	67.8	9.2			
	35	26.5	63.8	9.5			
	46	31.7	59.5	8.9			
	50	34.7	56.0	9.3			
	56	35.8	55.3	8.6			
P_3	0	1.4	12.3	84.8	1.7		
	1	4.5	16.4	73.7	5.4		
	1.8	6.9	21.3	64.6	7.3		
	2.7	9.3	23.4	59.3	8.3		
	5	13.2	32.5	45.7	8.4		
P_4	0	2.8	3.0	4.7	88.0	1.1	0.2
	1.5	7.8	4.1	15.7	69.5	1.9	0.9
	3	12.2	6.4	22.5	55.4	1.8	1.6
	4.7	16.6	9.2	26.8	43.5	1.6	2.1
	6	19.9	11.4	28.6	36.2	1.4	2.4
	7.5	23.1	14.0	29.4	29.8	1.1	2.5
	9.3	26.5	17.1	29.6	23.7	0.6	2.3

[a] See Ref.9.

the concentration of each phosphate at various times is presented in Table 1. When the concentration of the triphosphate to be hydrolyzed and of the equimolar Al^{3+} ion was decreased to 5×10^{-4} mol dm^{-3}, the maximum yield of tetraphosphate was 4 %(as P). Similarly, the hydrolysis products of tetraphosphate, of which initial concentration was 2.5×10^{-3} mol dm^{-3} in the presence of equimolar Al^{3+} were analyzed and the formation of pentaphosphate was confirmed; the chromatograms are shown in Figure 2. The maximum yield was about 1.9 %(as P)(Table 1). Linear phosphates which contain one more P atom in their molecule than the parent phosphates were found in the hydrolysis samples of the parent phosphates. The mechanism for the formation of tetraphosphate during the hydrolysis reaction of triphosphate was speculated to be as follows. At first, triphosphate is hydrolyzed to di- and monophosphate; these phosphates can be regarded as free radicals produced immediately after the scission of the P-O-P bond in the triphosphate(Eq.(1)).

$$P_3 \rightarrow P_2^* + P_1^* \quad (1) \qquad P_1^* + P_3 \rightarrow P_4 \quad (2)$$

The residence time of P_1^*(monophosphate radical) or P_2^*(diphosphate radical) thus formed around the Al^{3+} ion is considered to be relatively long, so that the probability of the attacking of these radicals by the triphosphate, which is also attracted by the same Al^{3+} ion, is increased. However, under our experimental conditions one might speculate that the probability of the attacking of P_2^* by P_3 is very low or that the life time of P_2^* is very short. The above mechanism is derived from the following experimental results. The presence of a near-equimolar Al^{3+} ion was necessary for this "condensation reaction". The "condensation reaction" occurred only during the hydrolysis reactions of di-, tri- or tetraphosphate, but did not occur under the presence of other metal ions such as copper(II), nickel(II) or magnesium(II) ions. The slow exchange of the phosphate ligands which coordinate with Al^{3+} ion may enhance the probability of the collision between the ligands around the Al^{3+} ion.

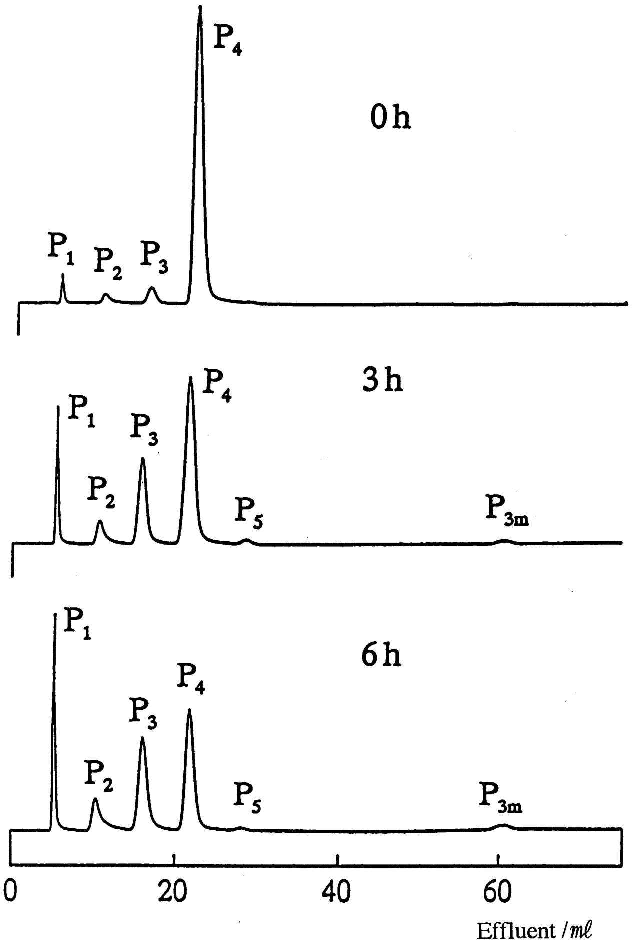

Figure 2. Chromatograms of the degradation products of tetraphosphate.

In this paper, cyclo- and linear phosphates are designated as P_{nm} and P_n, respectively, where n is the number of phosphorus atoms per molecule.

References and Notes

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