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MECHANOCHEMICAL CHANGE OF TRISODIUM ISOHYPOPHOSPHATE TETRAHYDRATE BY GRINDING

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Mechanochemical change of trisodium isohypophosphate tetrahydrate ($\overset{3}{P}$-O-$\overset{5}{P}$), one of the lower phosphorus oxoacid salts, was investigated by analysis of species of phosphorus oxoanions. On grinding of $\overset{3}{P}$-O-$\overset{5}{P}$-salt, the P-O-P linkages were broken to give phosphonate and pyrophosphate. This shows that the decomposition of $\overset{3}{P}$-O-$\overset{5}{P}$-salt and the recombination of two phosphate radicals produced by grinding, occurred due to grinding.

We have investigated the effect of grinding on the various salts of phosphorus oxoanions with the oxidation numbers of five.1) The salts of the lower phosphorus oxoacids are not appreciably investigated except for diphosphonate ($\overset{3}{P}$-O-$\overset{3}{P}$) and hypophosphate ($\overset{4}{P}$-$\overset{4}{P}$).2,3) In this work, therefore, the changes of the molecular species by grinding of trisodium isohypophosphate tetrahydrate ($\overset{3}{P}$-O-$\overset{5}{P}$) were primarily examined. As this salt was somewhat hygroscopic and became progressively more so with the grinding time, it was ground in a dry nitrogen gas atmosphere. Trisodium isohypophosphate tetrahydrate ($\overset{3}{P}$-O-$\overset{5}{P}$), $Na_3P_2HO_6\cdot 4H_2O$, was prepared according to the method given in the literarure.4) The analytical procedure, grinding method, and apparatus used in the present study were essentially the same as those used in the previous papers.2,3,5)

Figure 1 shows the phosphorus distribution in the ground samples. The amount of each species of the phosphorus oxoanions was determined by isotachophoresis.6,7) Samples used for the grinding included orthophosphonate ($\overset{3}{P}$), orthophosphate ($\overset{5}{P}$), and pyrophosphate ($\overset{5}{P}$-O-$\overset{5}{P}$) as impurities because the removal of them by the recrystallization from water was very difficult.[4)] It can be seen from Fig. 1 that, with the progress of the grinding, $\overset{3}{P}$-O-$\overset{5}{P}$ almost linearly decreased, while $\overset{3}{P}$ and $\overset{5}{P}$-O-$\overset{5}{P}$ increased, and that the amount of P atom of severed $\overset{3}{P}$-O-$\overset{5}{P}$ was equal to those of $\overset{3}{P}$ and $\overset{5}{P}$-O-$\overset{5}{P}$ stoichiometrically. This finding shows that the cleavage and recombination of P-O-P linkages occurred upon grinding as shown by the following equation.

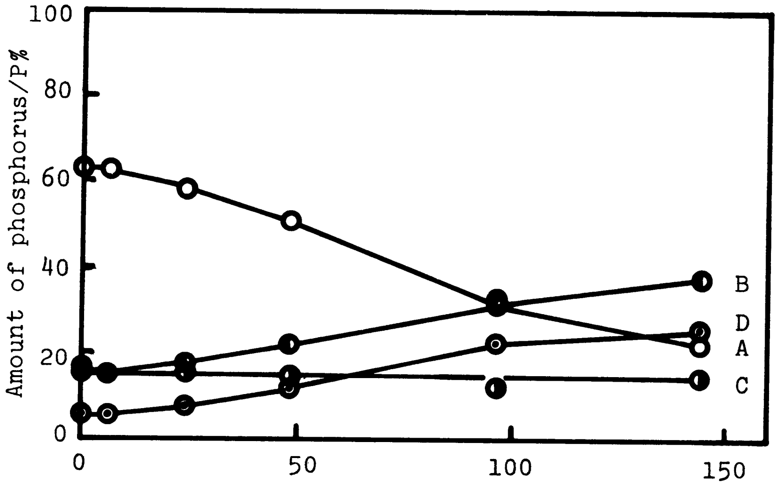


Fig. 1. Changes in phosphorus distribution in ground trisodium isohypophosphate. A; $\overset{3}{P}$-O-$\overset{5}{P}$, B; $\overset{3}{P}$, C; $\overset{5}{P}$, D; $\overset{5}{P}$-O-$\overset{5}{P}$.

$$2\ \overset{3}{P}\text{-O-}\overset{5}{P} \xrightarrow{\text{Grinding}} 2\ \overset{3}{P} + \overset{5}{P}\text{-O-}\overset{5}{P}$$

Figure 2 shows the DTA and TG curves of the samples ground for the various times. In Fig. 2, the exo- and endothermic peaks at 400 and 150 °C are due to the oxidation of $\overset{3}{P}$-O-$\overset{5}{P}$-salt to $\overset{5}{P}$-O-$\overset{5}{P}$-salt and the condensation of $\overset{3}{P}$-salt ($NaHPHO_3$) produced by severing of $\overset{3}{P}$-O-$\overset{5}{P}$ linkage to $\overset{3}{P}$-O-$\overset{3}{P}$-salt, respectively. On the other hand, three small peaks at 390, 250, and 190 °C are due to $\overset{3}{P}$- and $\overset{5}{P}$-salts, which were present as the impurities.
The large endothermic peak accompanied with weight loss near 100 °C is due to the dehydration of the water of crystallization in $\overset{3}{P}$-O-$\overset{5}{P}$-salt. As shown in Fig. 2, the tetramolecular water of

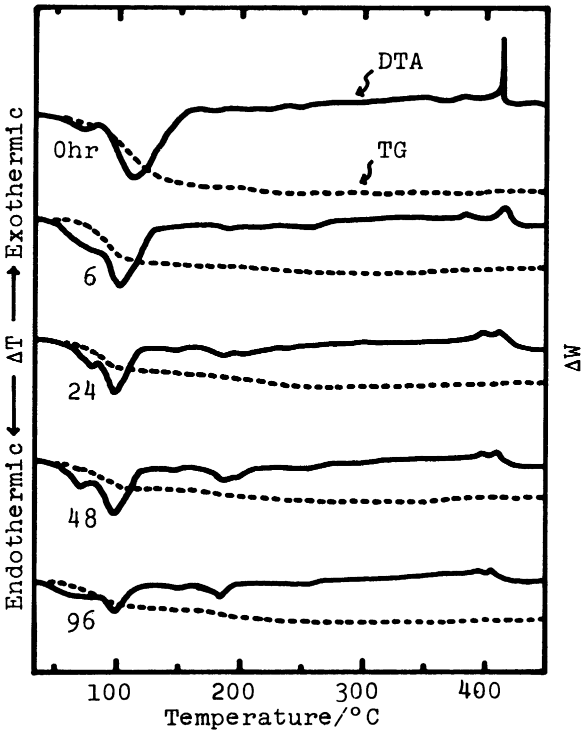
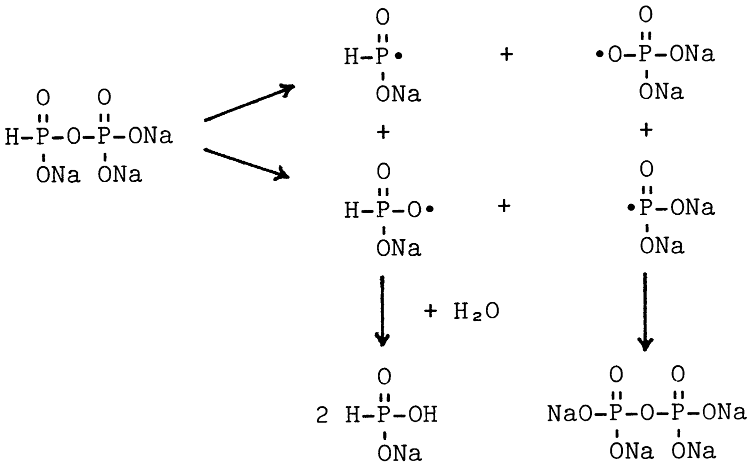


Fig. 2. DTA and TG curves of the ground $Na_3P_2HO_6 \cdot 4H_2O$.

crystallization was gradually lost with grinding; 0 hr (23.9%), 6 hr (14.8%), 24 hr (11.1%), and 96 hr (9.8%). This dehydration resulted in the severing of $\overset{3}{P}$-O-$\overset{5}{P}$ linkage. When $Na_3P_2HO_6 \cdot 4H_2O$ was sucked dry at 50 °C, the $\overset{3}{P}$-O-$\overset{5}{P}$ linkage was severed as well as the water of crystallization was lost. Therefore, the intermolecular hydrogen bond between the water of crystallization and the phosphorus oxoanion serves to stabilize the $\overset{3}{P}$-O-$\overset{5}{P}$ bond in addition to the crystal structure. The X-ray diffraction patterns showed that the crystalline $\overset{3}{P}$-O-$\overset{5}{P}$-salt was rapidly converted into amorphous phase due to grinding.

From the results described above, we may propose the following mechanism.



We could not determine which linkages of $\overset{3}{P}$-O or O-$\overset{5}{P}$ to be severed. If the $\overset{3}{P}$-O-$\overset{5}{P}$ linkage was severed at random, $NaPHO_2\cdot$ and $NaPHO_3\cdot$ radicals produced react with water molecule to give phosphonate, or $Na_2PO_4\cdot$ and $Na_2PO_3\cdot$ radicals recombine with each other to form pyrophosphate. We are now investigating the presence of these radicals. On the other hand, as shown in the following equations, the mechanism of the formation of pyrophosphate via Na_2HPO_4 was not considered because the $\overset{5}{P}$-O-$\overset{5}{P}$-salt was not entirely produced even if Na_2HPO_4 was ground.

$$Na_3P_2HO_6 \quad + \quad H_2O \xrightarrow{\text{Grinding}} Na_2PHO_3 \quad + \quad Na_2HPO_4$$

$$2\ Na_2HPO_4 \xrightarrow{\text{Grinding}} Na_4P_2O_7 \quad + \quad H_2O$$

In general, the P-O-P linkages of condensed phosphates were cleavaged to give the shorter-chain phosphates upon grinding except that some species were condensed to give the long-chain phosphates.[8-12] In the present study, it is very interesting that the severed phosphate radicals recombined stoichiometrically to give pyrophosphate.

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