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# Studies of the Formation Mechanism of Sodium Tripolyphosphate from Orthophosphates by the Use of Radioisotopes

Takaya IIDA, Nobuharu TAKAI, and Takeo YAMABE

*The Institute of Industrial Science, The University of Tokyo, Roppongi, Minato-ku, Tokyo*

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The reaction process of an equimolar mixture of mono- and disodium orthophosphates was examined to serve as a reference for the considerations of the mechanism of the formation of sodium tripolyphosphate. Differential thermoanalysis, thermogravimetric analysis, X-ray diffraction analysis and thin-layer chromatographic analysis were done. Particularly, the reaction mechanisms (the formation of liquid $Na_3HP_2O_7$, *etc.*) were also examined by the use of the "$^{32}P$" radioisotope. The reaction process is as follows:

$$\left.\begin{array}{l} NaH_2PO_4 \longrightarrow Na_2H_2P_2O_7 \\ Na_2HPO_4 \longrightarrow Na_4P_2O_7 \end{array}\right\} \rightleftarrows Na_3HP_2O_7\,(liq.) \longrightarrow \left\{\begin{array}{l} Na_2H_2P_2O_7 \\ Na_5P_3O_{10}\,(I) \end{array}\right.$$

$$\longrightarrow Na_5P_3O_{10}\,(I) + Na_5P_3O_{10}\,(II) + NaPO_3\,(II)$$

A feedback phenomenon of $Na_2H_2P_2O_7$ was observed.

Condensed phosphates have interested many investigators as inorganic poly-substances. Among them, sodium tripolyphosphate is industrially most important, because it is used in large quantities as *e. g.*, a builder of synthetic detergents.

In general, sodium tripolyphosphate is prepared from a mixture of orthophosphates with a $Na_2O/P_2O_5$ mole ratio of 5/3 by thermal dehydration:

$$2Na_2HPO_4 + NaH_2PO_4 \longrightarrow Na_5P_3O_{10} + 2H_2O \quad (1)$$

In the intermediate step, tetrasodium pyrophosphate and sodium acid pyrophosphate are formed at first.[1] T. Seiyama *et al.* proposed that the reaction process of the formation of sodium tripolyphosphate from pyrophosphates mixture was as follows:[2,3]

$$Na_4P_2O_7 + Na_2H_2P_2O_7 \longrightarrow 2Na_3HP_2O_7\,(liq.) \quad (2)$$

$$2Na_3HP_2O_7 \longrightarrow Na_5P_3O_{10}\,(I) + 1/2Na_2H_2P_2O_7 + 1/2H_2O \quad (3)$$

$$1/2Na_2H_2P_2O_7 \longrightarrow 1/4Na_4H_2P_4O_{13} + 1/4H_2O \quad (4)$$

$$1/4Na_4H_2P_4O_{13} + Na_4P_2O_7 \longrightarrow Na_5P_3O_{10}\,(II) + 1/4H_2O \quad (5)$$

In the thermal decomposition of $Na_3HP_2O_7$, reaction (3) takes place at first; then the following reaction occurs:[4]

$$Na_2H_2P_2O_7 \longrightarrow 2NaPO_3\,(II) + H_2O \quad (6)$$

Studies of the thermal reaction of equimolar mixtures of mono- and disodium orthophosphates did not concern the detailed reaction process.[5]

1) J. W. Edwards and A. H. Herzog, *J. Amer. Chem. Soc.*, **79**, 3647 (1957).
2) T. Seiyama, A. Ichikawa, and T. Inoue, *Kogyo Kagaku Zasshi*, **66**, 573 (1963).
3) T. Seiyama, A. Kato, T. Ikeda, and H. Miyazaki, *ibid.*, **68**, 449 (1965).
4) T. Seiyama, A. Ichikawa, and T. Inoue, *ibid.*, **66**, 5 (1963).
5) F. E. Hubbard, *Ind. Eng. Chem.*, **41**, 2908 (1949).

Studies of the thermal reaction of equimolar mixtures of mono- and disodium orthophosphates were also performed; particularly, the reaction mechanisms (the formation of liquid $Na_3HP_2O_7$ from a pyrophosphates mixture, etc.) were investigated by the use of the "$^{32}P$" radioisotope.

## Experimental

*Reagents.* The $Na_2HPO_4$ was a commercially available substance (Analytical grade; Wako Pure Chemical Industries, Ltd.); it was dried at 110°C. The $NaH_2PO_4$ was prepared from commercial $NaH_2PO_4 \cdot 2H_2O$ (Analytical grade; Wako) by thermal dehydration at 110°C.

*Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA).* DTA and TGA were done simultaneously by the use of a Thermoflex (DG-C1H, Rigaku-Denki Co., Ltd.). Heating rates were 2.5°C/min and 5°C/min, respectively.

As to quenched samples, X-ray diffraction analysis and chromatographic analysis were done. The quenched samples were prepared as follows;

Equimolar mixtures of mono- and disodium orthophosphates were heated to the appointed temperature at the heating rate of 2.5°C/min by the use of the Thermoflex, and then the heated mixtures were rapidly quenched. (Sample No. 1: 223°C, Sample No. 2: 303°C, Sample No. 3: 380°C).

*X-Ray Diffraction Analysis.* The X-ray diffraction work was done by the use of a Geigerflex (D-9C, Rigaku-Denki Co., Ltd.). The X-ray diffraction analysis was made by the use of the diffraction angles[6] shown in Table 1. Cu$K\alpha$ radiation was used.

Table 1. X-ray diffraction angles used in X-ray diffraction analysis

| Phosphates | $2\theta$ (°) |
|---|---|
| $Na_5P_3O_{10}$ (I) | 21.8, 29.1 |
| $Na_5P_3O_{10}$ (II) | 24.8 |
| $Na_4P_2O_7$ | 26.4 |
| $Na_3P_3O_9$ | 26.2 |
| $NaPO_3$ (II) | 30.9 |
| $Na_2H_2P_2O_7$ | 30.5, 25.9 |

*Chromatographic Analysis.* The thin-layer chromatographic analysis was done using acidic and basic developing solvents.

*Acidic Solvents.*[7] Isopropanol-60 m*l*; water-40 m*l*; trichloroacetic acid-4 g; ammonia water(28%)-0.25 m*l*; and acetic acid-1.5 m*l*.

*Basic Solvents.*[9] Isopropanol-40 m*l*; isobutanol-20 m*l*; ammonia water(28%)-1 m*l* and water-39 m*l*.

The $Na_2HPO_4$ and $NaH_2PO_4$ were weighed accurately to make them easy to mix, and then they were enclosed in polyethylene tubes and neutron bombardment was made using JRR-2 ($\phi_n = 8 \times 10^{13}$ n/cm$^2$·sec; 5 min; reactor temperature) at the Japan Atomic Energy Research Institute, Tokai, Ibaraki.

The formation of phosphorus oxyacids and of polyphosphates other than phosphates is thought to be fairly slight under these conditions,[10] so we did not consider them.

One mole of $Na_2HPO_4$ was mixed with one mole of neutron applied $NaH_2PO_4$ (Sample A), and one mole of $NaH_2PO_4$, with one mole of neutron applied $Na_2HPO_4$ (Sample B). The two samples were simultaneously heated from room temperature up to the temperature of 380°C at the heating rate of about 3°C/min in quartz tubes in an electric furnace.

*Radioactivity Measurements.* Sample A and Sample B were dissolved in water, and the undissolved substances were separated by the use of a glass filter. The radioactivity of the undissolved substances was measured using a G.M. counter (SA-30, Ten Kogyo).

## Results and Discussion

The DTA and TGA curves of an equimolar mixture of $Na_2HPO_4$ and $NaH_2PO_4$ are shown in Fig. 1.

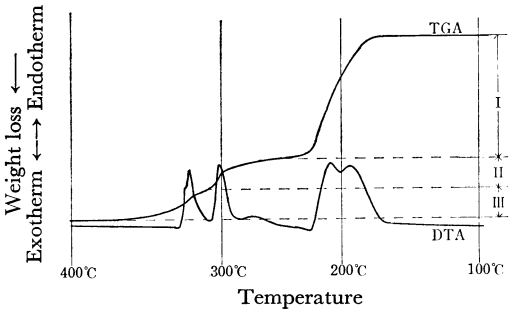



Fig. 1. DTA and TGA curves of equimolar mixture of $Na_2HPO_4$ and $NaH_2PO_4$.
Heating rate: 2.5°C/min Sample weight: 389 mg
I: obsd −25.9 mg, calcd −26.7 mg
II: obsd −6.6 mg, calcd −6.7 mg
III: obsd −6.6 mg, calcd −6.7 mg

According to X-ray diffraction analysis and chromatographic analysis, the main substances existing in the quenched samples are as follows:

Sample No. 1: $Na_2H_2P_2O_7$ and $Na_4P_2O_7$

Sample No. 2: $Na_5P_3O_{10}$ (I), and $Na_2H_2P_2O_7$

Sample No. 3: $Na_5P_3O_{10}$ (I), $Na_5P_3O_{10}$ (II), and $NaPO_3$ (II)

We could not separate the endothermic reactions with peaks at 193°C and 210°C. DTA was done on mixtures of orthophosphates in different proportions ($Na_2HPO_4 : NaH_2PO_4 = 2:1$, $1:1$, and $1:2$ (mole ratio)). The results are shown in Fig. 2. It is thought that the endothermic reaction with a peak at 193°C corresponds to the reaction (7), and that the one at 210°C corresponds to the reaction (8):

$$2NaH_2PO_4 \longrightarrow Na_2H_2P_2O_7 + H_2O \quad (7)$$

$$2Na_2HPO_4 \longrightarrow Na_4P_2O_7 + H_2O \quad (8)$$

The endothermic reaction with the peak at 301°C is considered to correspond to this reaction:

$$\left.\begin{matrix} Na_2H_2P_2O_7 \\ Na_4P_2O_7 \end{matrix}\right\} \longrightarrow Na_5P_3O_{10}\,(I) + 1/2Na_2H_2P_2O_7 + 1/2H_2O \quad (9)$$

6) S. Ohashi, ed. "Mukikagaku-Zensho" IV-6, "Phosphorus," Maruzen, Tokyo (1965), p. 49.

7) A solvent slightly modified from the solvent in Ref. 8 was used.

8) E. Thilo and W. Feldmann, *Z. Anorg. Allg. Chem.*, **298**, 316 (1959).

9) E. Karl-Kroupa, *Anal. Chem.*, **28**, 1091 (1956).

10) S. Ohashi *et al.*, "KURRI-TR-52 (Kyoto University Reactor Research Institute Technical Reports)," (1968), p. 23.

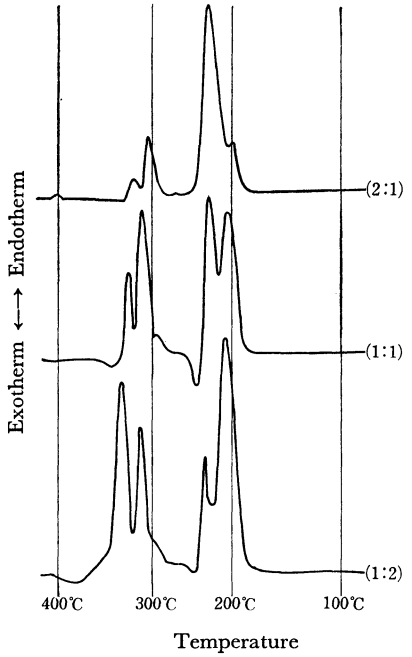



Fig. 2. DTA curves of mixtures of orthophosphates in different proportion ($Na_2HPO_4$: $NaH_2PO_4$= 2:1, 1:1, and 1:2 (mole ratio)).
Heating rate: 5°C/min

Further, the endothermic reaction with the peak at 321°C is considered to correspond to this reaction:

$$1/2Na_2H_2P_2O_7 \longrightarrow NaPO_3\,(II) + 1/2H_2O \qquad (10)$$

The final products were sodium tripolyphosphate and sodium metaphosphate (type II). The former is soluble in water, while the latter is insoluble in water. Therefore, these two substances can be separated when the final products are dissolved in water and filtered.

Table 2. Results of radioactivity measurements

| Sample | before filtration ($Na_5P_3O_{10}$+$NaPO_3$ (II)) | after filtration ($NaPO_3$(II)) |
|---|---|---|
| A | 12150±100 cpm | 3374±194 cpm |
| B | 6909±240 cpm | 1383± 27 cpm |

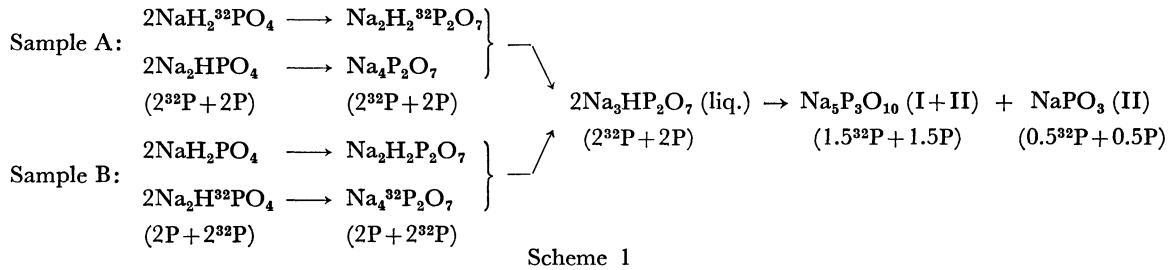
The results of the radioactivity measurements are shown in Table 2. As for sample A, the ratio of the radioactivity after filtration ($NaPO_3$(II)) to that before filtration ($Na_5P_3O_{10}$+$NaPO_3$(II)) was about 1 : 3.6. As for Sample B, the ratio was about 1 : 5.0.

If all of the $Na_2H_2P_2O_7$ and $Na_4P_2O_7$ react to liquid $Na_3HP_2O_7$ and are then converted to $Na_5P_3O_{10}$(I) and $Na_2H_2P_2O_7$, the ratio should be 1 : 4 (Scheme 1). However, the results do not agree with this value. It is, therefore, better to think of some different processes in this case. Two processes can be considered.

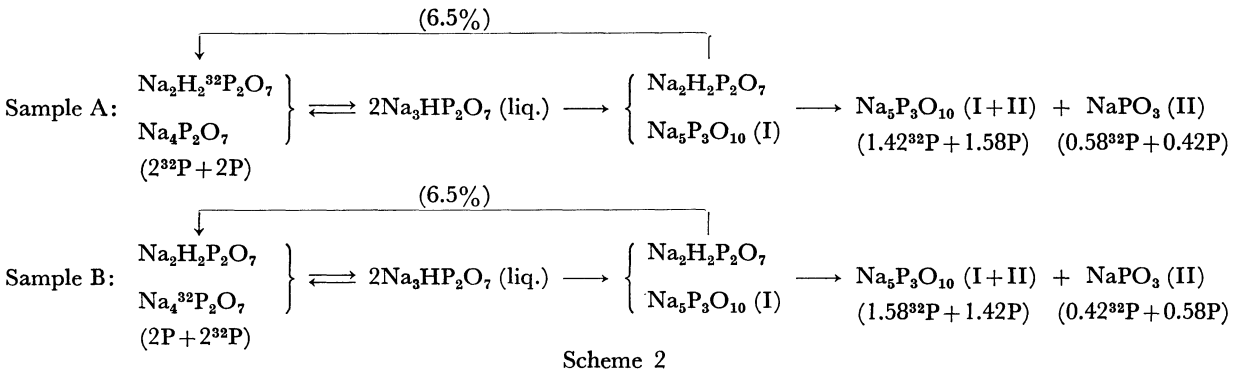
First, it is thought that the decomposition of liquid $Na_2HP_2O_7$ to $Na_2H_2P_2O_7$ and $Na_4P_2O_7$ occurs,[4] but that the ratio should be 1 : 4 if there is no feedback phenomenon of $Na_2H_2P_2O_7$ (this will be discussed below).

Second, it is thought that the formation of liquid $Na_3HP_2O_7$ from $Na_2H_2P_2O_7$ and $Na_4P_2O_7$ is slow, that the conversion to $Na_5P_3O_{10}$(I) and $Na_2H_2P_2O_7$ is fast, and that the feedback phenomenon of $Na_2H_2P_2O_7$ occurs. If only one feedback of $Na_2H_2P_2O_7$ is assumed, it is calculated that about 6.5% of the $Na_2H_2P_2O_7$ is fed back. (For Sample A, the ratio is about 1 : 3.4, and for Sample B, the ratio is about 1 : 4.8 (Scheme 2).)

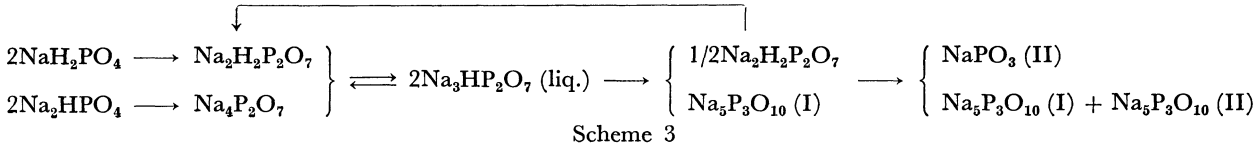
The $Na_5P_3O_{10}$(II) in Sample No. 3 is thought to be formed by the conversion of the $Na_5P_3O_{10}$(I) in Sample No. 2.[1] The reaction precess is shown in Scheme 3.




Scheme 1




Scheme 2




Scheme 3