[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

# The Transition between the Low- and the High-Temperature Form of Sodium Tripolyphosphate

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Sodium tripolyphosphate was heated in closed tubes with 0.1% $Na_5P_3O_{10}\cdot 6H_2O$, corresponding to 0.023% $H_2O$ for periods of about a month. Under these conditions at 409° and below $Na_5P_3O_{10}$ I changed to $Na_5P_3O_{10}$ II, while $Na_5P_3O_{10}$ II remained unchanged; and at 425° $Na_5P_3O_{10}$ II changed to $Na_5P_3O_{10}$ I, while $Na_5P_3O_{10}$ I remained unchanged. The two forms are enantiotropic with a transition temperature of 417 ± 8°.

In a previous paper[1] it was stated: "$Na_5P_3O_{10}$ has two crystalline modifications, but the conditions for their formation are not clear. The low-temperature[2] form, II, is obtained when a melt is cooled slowly to about 550° and removed from the furnace, after which the melt frequently spontaneously disintegrates, as it approaches room temperature, into a powder of $Na_5P_3O_{10}$ (II). This form can be prepared by heating $Na_5P_3O_{10}\cdot 6H_2O$ at 350°, but the product is not as well crystallized as that obtained by spontaneous inversion. Attempts to fix a transition temperature I ⇄ II failed. When form II was heated with water in a pressure vessel at temperatures up to 400° and 750 p.s.i. pyrophosphate was formed. The transition II → I takes place quickly at 535°, slowly at 500°, in one week at 438° and not in 5 weeks at 380°. In these experiments the two forms were placed side by side, but in no case did form I change to II. We have not been able to change I to II by any treatment except the spontaneous change on cooling described above."

After the publication of that paper, Dr. Oscar T. Quimby suggested that, although the amounts of water used in the experiments described above caused formation of pyrophosphate, a trace of moisture might prove effective and suggested the use of a sealed tube containing 0.1% by weight of $Na_5P_3O_{10}\cdot 6H_2O$. Dr. Quimby also supplied a quantity of the hydrate.

Two sets of experiments were made with sodium tripolyphosphate containing 0.1% $Na_5P_3O_{10}\cdot 6H_2O$, which proportion gives 0.023% by weight of $H_2O$; one set with $Na_5P_3O_{10}$ I, the other with $Na_5P_3O_{10}$ II. The $Na_5P_3O_{10}$ I was made by crystallizing the glass at 500°, cooling, powdering to pass a 66-mesh sieve, and holding for a week at 500°. The $Na_5P_3O_{10}$ II resulted from the spontaneous transformation with dusting of a 25 g. melt. In each case about 10 g. of the mixture was prepared and mixed by sieving five times through 98-mesh bolting cloth. Samples of about 1.5 g. were sealed in tubes of Corning 172 glass (10 mm. o.d., 7.5 mm. i.d.), which about half-filled the tubes, and were heated in an electrically heated and controlled tube furnace, of the type used in this Laboratory for quenching, with a bore of 1/2 in. The measuring Pt–Pt 10% Rh thermocouple was placed between the tube and the inner wall of the furnace, at about the middle of the powder. Temperature was continuously recorded, and the recorder was frequently checked with a White-type Leeds and Northrup potentiometer. The furnace control was such that the deviation of temperature for a month-long run was about 2°.

The results of the various experiments are summarized in Table I. It was found that runs of short duration were not sufficient to complete the transformation. For example, in 5 days at 360° a tube originally containing $Na_5P_3O_{10}$ I was a mixture of I and II. The run of $Na_5P_3O_{10}$ II at 409° for 50 days is listed in the table as unchanged, but the X-ray pattern was greatly sharpened by the long heat treatment. It will be seen that, at 409° and below, $Na_5P_3O_{10}$ I was changed to $Na_5P_3O_{10}$ II, but $Na_5P_3O_{10}$ II was unchanged; while at 425° form I was unchanged and form II was changed to form I. The two forms must be enantiotropic with a transition temperature of 417 ± 8°.

TABLE I

CLOSED TUBE EXPERIMENTS IN WHICH 0.1% $Na_5P_3O_{10}\cdot 6H_2O$ WAS ADDED TO THE CRYSTALLINE TRIPOLYPHOSPHATE

| Temp. (°C.) | Duration (days) | Condition |
|---|---|---|
| A. The tube contained $Na_5P_3O_{10}$ I | | |
| 320 | 40 | Form II |
| 360 | 33 | Form II |
| 390 | 60 | Form II |
| 409 | 32 | Form II |
| 425 | 30 | Unchanged |
| B. The tube contained $Na_5P_3O_{10}$ II | | |
| 390 | 30 | Unchanged |
| 409 | 50 | Unchanged |
| 425 | 34 | Form I |

(1) G. W. Morey, F. R. Boyd, Jr., J. L. England and W. T. Chen, THIS JOURNAL, **77**, 5008, col. 2, para. 2 (1955).

(2) E. P. Partridge, V. Hicks and G. W. Smith, *ibid.*, **63**, 454 (1941).

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