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Studies of the Grinding of Condensed Phosphates. IV. Grinding of Sodium Trimetaphosphate at Low Pressure

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The change in sodium trimetaphosphate by grinding at low pressure was examined by the X-ray diffraction method and paper chromatography. The crystalline sodium trimetaphosphate became amorphous more rapidly when ground at low pressure than in dry air or nitrogen gas, and in these cases the chain phosphates higher than triphosphate were produced in addition to ortho-, pyro- and tri-phosphates.

In the previous papers,[1,2] it has been reported that the P–O–P linkages of cyclic sodium trimetaphosphate were severed to the chain phosphates due to grinding and the chain-length of some long-chain phosphates such as lithium, sodium and potassium polyphosphates decreased as a result of the cleavage of the P–O–P linkages upon grinding.

It was reported by Baramboim[3] that organic high polymers such as polystyrene depolymerize to the shorter-chain molecules upon grinding in the manner similar to the previous papers.[1,2] On the contrary, Kargin *et al.*[4] reported that styrene and other monomers polymerize by mechanical treatment.

In the case of phosphates, the possibility of producing the longer-chain phosphates by condensation can be anticipated. As the polymerization of phosphates is a condensation reaction in which water molecules are expelled, this reaction will be affected by the water molecules and so sodium trimetaphosphate was ground at low humidity and at low pressure, namely, one to several mmHg.

Experimental

Materials. Trisodium dihydrogen triphosphate, $Na_3H_2P_3O_{10}\cdot 1.5H_2O$, was prepared by the addition of alcohol to the aqueous solution of sodium salt which was adjusted to pH 4.6 with perchloric acid. The X-ray diffraction pattern of the precipitate[*1] obtained was

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[1] Part I: I. Motooka, G. Hashizume and M. Kobayashi, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **87**, 255 (1966).

[2] Part II: I. Motooka, G. Hashizume and M. Kobayashi, *ibid.*, **87**, 953 (1966).

[3] N. K. Baramboim, *Zh. Fiz. Khim.*, **32**, 432 (1958).

[4] N. A. Plate and V. A. Kargin, *J. Polymer Sci.*, **62**, 1027 (1962).

[*1] This precipitate contained ortho- and pyrophosphates of 10 to 20% in the analysis of paper chromatography.

identical with Corbridge's data.[5]

The preparation of sodium trimetaphosphate, $Na_3P_3O_9$, disodium dihydrogen pyrophosphate, $Na_2H_2P_2O_7$, and monosodium dihydrogen orthophosphate, NaH_2PO_4, has been described in a previous paper.[1]

Apparatus. The apparatus used in grinding was an Ishikawa's vacuum grinder (AGZ-type) and, in case of need, the same as in the previous paper[2] was used.

Procedure. One gram of phosphate was ground for a difinite time. The atmosphere during grinding was controlled in the following way. (1) In dry air: after the air in the grinding apparatus had been removed with a vacuum pump, the air dried by passing it successively through concentrated sulfuric acid, silica gel and phosphorus pentoxide was introduced into the apparatus. New phosphorus pentoxide was always provided in the apparatus. The relative humidity in it was 5 to 10% by a hair hygrometer. (2) In nitrogen gas: after the air had been removed, the apparatus was filled with dry nitrogen gas. New phosphorus pentoxide was also provided in it. The relative humidity was the same as in (1). (3) At low pressure: sample was ground while evacuating with a vacuum pump to below 5 mmHg pressure. The relative humidity was below 5% by a hair hygrometer.

Results and Discussion

Grinding of Sodium Trimetaphosphate at Low Pressure. As stated in the previous paper,[6] water molecules participate in the mechanism of the change which takes place when sodium trimetaphosphate is ground. Therefore, in order to investigate further the effect of water molecules, the grinding was carried out in an atmosphere evacuated to below 5 mmHg pressure as one method for reducing the water molecules.

Figure 1 shows the changes in X-ray diffraction patterns of sodium trimetaphosphate due to grinding in various atmospheres. It can be seen that the effect of grinding at low pressure is larger than that of grinding in dry air or nitrogen gas. For example, although the diffraction lines of sodium trimetaphosphate remain even after grinding for 6 hr in the dry air and nitrogen gas, the product ground for 6 hr at low pressure is amorphous. As regards the relative humidity, this result agrees with that of the previous paper[6]—that is, the grinding effect decreases with increase in relative humidity.

Rehbinder *et al.*[7] have investigated the effect of water on grinding of quartz, and reported that more amorphous layer was produced as the water content decreased. There is a good agreement between their results and ours. The results described above, however, can not be interpreted simply as due to low humidity since factors[*2] other than water molecules must be taken into account in the case of low pressure.

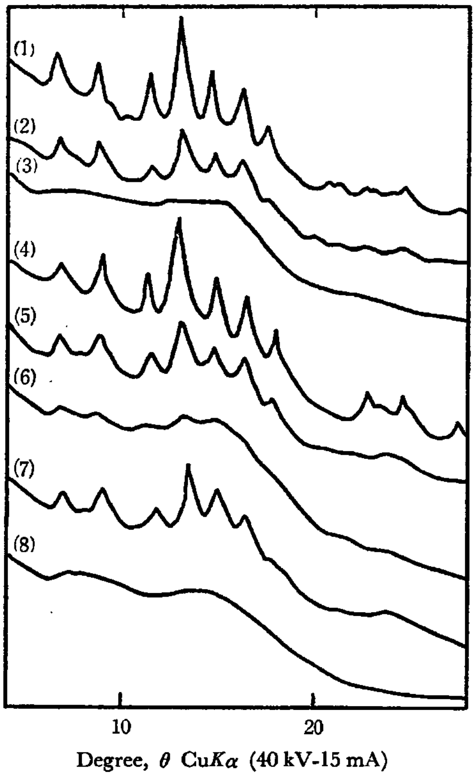

Fig. 1. X-ray diffraction patterns of $Na_3P_3O_9$ in various atmospheres.

(1) 3 hr grinding in dry air
(2) 6 hr grinding in dry air
(3) 24 hr grinding in dry air
(4) 3 hr grinding in nitrogen gas
(5) 6 hr grinding in nitrogen gas
(6) 9 hr grinding in nitrogen gas
(7) 3 hr grinding at low pressure
(8) 6 hr grinding at low pressure

The results of analyses of these ground samples by paper chromatography are given in Table 1.[*3] The rate of decrease of trimetaphosphate molecules by grinding at low pressure is the fastest and this supports the results of the change in X-ray diffraction patterns in Fig. 1. They differ from those in the preceding paper[1] in that considerable tetra- and

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5) E. C. Corbridge and F. R. Tromans, *Anal. Chem.*, **30**, 1101 (1958).

6) Part III: I. Motooka, G. Hashizume and M. Kobayashi, This Bulletin, **40**, 2095 (1967).

7) P. A. Rehbinder and G. S. Chodakow, *Silikattechn.*, **13** [6], 200 (1962).

[*2] For example, the flow of air in the apparatus.[8]

8) G. Jimbo, *Hyomen* (*Surface*), **1**, 47 (1963).

[*3] Although the grinders used in this experiment were of the Ishikawa type, the grinding effect—for example, the rate of production of amorphous substance or the distribution of the various kinds of phosphates—was affected by its kind (AG-type or AGA-type) and by the use of other grinder even if of the same kind. An example is given in Table 2. In the case of grinder of AGA-type No. 2, the grinding effect is largest, and especially the amounts of tetra- and higher-polyphosphates is largest at humidity of 20% and temperature of 20°C. Even in the case of the same grinder, the grinding effect becomes poor because of the defacement of the rotating shaft and the weakening of the force by which the pestle is pressed when used for a long time.

TABLE 1. DISTRIBUTION OF PHOSPHORUS AMONG THE SAMPLES GROUND AT VARIOUS ATMOSPHERES

Atmosphere	Grinding time (hr)	Analytical value by paper chromatography (%)				
		Ortho	Pyro	Tri	Tetra∼	Trimeta
Dry air	3	0	0	0	0	100
	6	0.2	0.8	1.0	0.4	97.6
	9	1.0	1.4	3.4	18.8	75.4
	24	7.1	6.9	7.1	45.4	33.5
Nitrogen gas	3	0	0	0	0	100
	6	3.0	5.4	3.5	17.5	70.6
	9	3.7	3.7	6.9	23.3	62.5
Low pressure	3	0	0.5	0.9	30.1	68.5
	6	0.3	0.5	2.8	41.2	55.2
	9	2.4	3.0	3.5	64.2	26.8

TABLE 2. EFFECT OF GRINDER

Grinder	Grinding time (hr)	Atmosphere		Analytical value (%)				
		Temp. (°C)	Humidity (%)	Ortho	Pyro	Tri	Tetra∼	Trimeta
AGA-type No. 1	72	30	40	5.0	5.9	9.7	0.4	79.1
AGA-type No. 2	72	30	40	12.7	12.8	30.3	4.0	40.2
AG-type	72	30	40	3.7	7.6	9.3	0.1	79.3
AGA-type No. 1	72	20	20	6.7	10.2	14.0	0.7	68.4
AGA-type No. 2	72	20	20	12.8	13.3	16.8	21.8	35.3

TABLE 3. DISTRIBUTION OF PHOSPHORUS AMONG THE SAMPLES GROUND AT LOW PRESSURE

Sample	Atmosphere	Grinding time (hr)	Analytical value (%)			
			Ortho	Pyro	Tri	Tetra∼
NaH_2PO_4	Low pressure	56	100	0	0	0
$Na_2H_2P_2O_7$	Low pressure	2	7.3	80.3	12.4	0
		6	17.1	49.8	20.8	12.4
	Dry air	6	5.8	94.2	0	0
$Na_3H_2P_3O_{10}$	Low pressure	3	10.3	37.7	40.7	11.3
		6	11.7	38.2	32.9	17.2
		9	13.3	37.8	26.3	22.7
	Relative humidity of 40%	6	14.5	28.0	57.5	0
		24	16.1	33.8	50.1	0
		48	20.1	44.0	35.9	0

higher- polyphosphates are produced in all cases of dry air, nitrogen gas and the evacuated state. This is due to the presence of smaller amounts of water molecules in the atmosphere of grinding and the following mechanisms can be assumed:

(1) Cyclic trimetaphosphates are severed to chain phosphates due to grinding and these chain phosphates are condensed to higher polyphosphates.

(2) The active molecules produced when the P-O-P linkages are severed are combined into longer-chain phosphates.

$$Na_3P_3O_9 \rightarrow Na_3P_3O_9: \qquad \text{(I)}$$

$$Na_3P_3O_9: + H_2O \rightarrow Na_3H_2P_3O_{10} \qquad \text{(II)}$$

$$Na_3H_2P_3O_{10} + H_2O \rightarrow Na_2H_2P_2O_7 + NaH_2PO_4 \qquad \text{(III)}$$

$$Na_2H_2P_2O_7 + H_2O \rightarrow 2NaH_2PO_4 \qquad \text{(IV)}$$

$$Na_kH_2P_kO_{3k+1} + Na_lH_2P_lO_{3l+1} \rightarrow Na_{k+l}H_2P_{k+l}O_{3(k+l)+1} + H_2O \quad (k,\ l = 1,\ 2,\ 3, \cdots) \qquad \text{(V)}$$

$$m\mathrm{Na_3P_3O_9}\colon + n\mathrm{Na_3P_3O_9}\colon \rightarrow \mathrm{Na_{3(m+n)}P_{3(m+n)}O_{9(m+n)}}\colon \qquad \text{(VI)}$$

$$\mathrm{Na_{3(m+n)}P_{3(m+n)}O_{9(m+n)}}\colon + \mathrm{H_2O} \rightarrow \mathrm{Na_{3(m+n)}H_2P_{3(m+n)}O_{9(m+n)+1}} \quad (m,\ n = 1,\ 2,\ 3,\cdots) \qquad \text{(VII)}$$

Equations (I) to (V) show the mechanism of (1) and Eqs. (I), (VI) and (VII) the mechanism of (2). It has been reported in the previous papers[1,6] that the reactions shown in Eqs. (I) to (IV) take place. It is considered that, in the present investigation, the reactions in Eqs. (V) and (VI) take place much more easily than the ones in Eqs. (II), (III) and (IV) since the amount of water molecules in atmosphere is small.

Grinding of Monosodium Dihydrogen Orthophosphate, Disodium Dihydrogen Pyrophosphate and Trisodium Dihydrogen Triphosphate at Low Pressure. In order to examine the possibility of Eq. (V), the grinding of NaH_2PO_4, $Na_2H_2P_2O_7$ and $Na_3H_2P_3O_{10}\cdot 1.5H_2O$ was studied in an atmosphere containing a small amount of water molecules. The X-ray diffraction patterns of NaH_2PO_4, $Na_2H_2P_2O_7$ and $Na_3H_2P_3O_{10}\cdot 1.5H_2O$ by grinding are shown in Figs. 2, 3 and 4, respectively. The X-ray diffraction pattern of NaH_2PO_4 ground for 56 hr is essentially identical with the original sample. $Na_2H_2P_2O_7$ becomes almost amorphous when ground for 6 hr at low pressure, but in dry air some diffraction lines of $Na_2H_2P_2O_7$ remain after grinding for 6 hr. $Na_3H_2P_3O_{10}$ changes similarly.

The distribution of various phosphates determined by paper chromatography is given in Table 3. Sample of NaH_2PO_4 ground for 56 hr is entirely orthophosphate. This is probably due to the fact

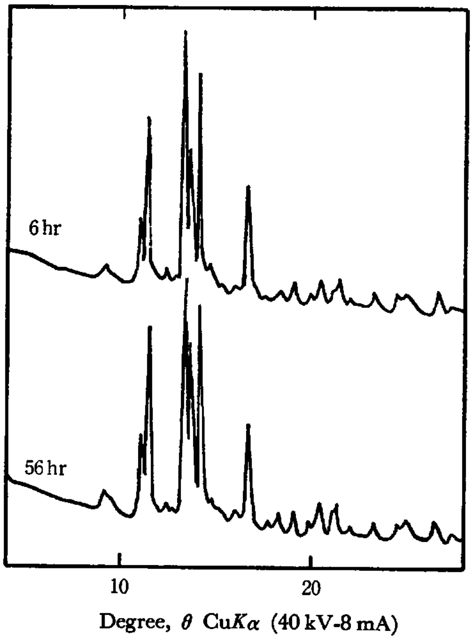

Fig. 2. X-ray diffraction patterns of NaH_2PO_4 ground at low pressure.
The numbers represent the grinding time.

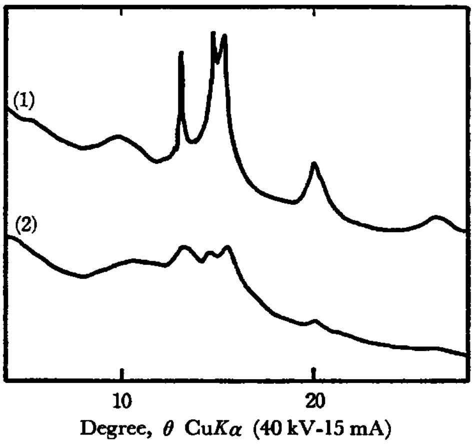

Fig. 3. X-ray diffraction patterns of $Na_2H_2P_2O_7$ ground in dry air and at low pressure.
(1) 6 hr grinding in dry air
(2) 6 hr grinding at low pressure

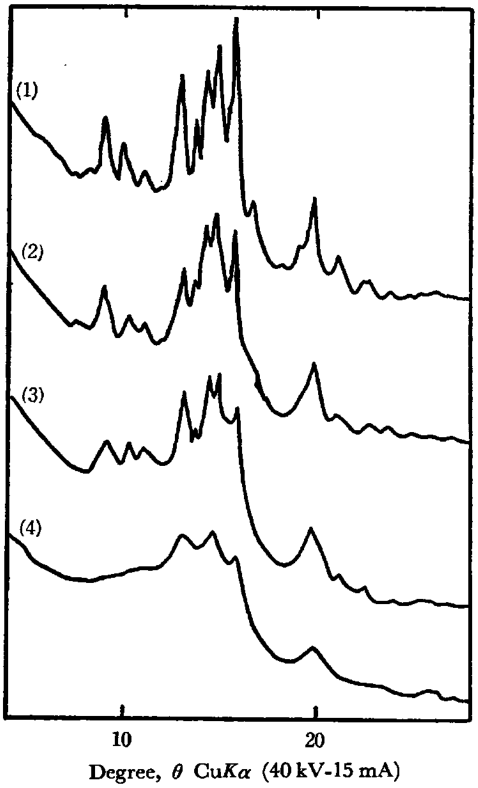

Fig. 4. X-ray diffraction patterns of the ground $Na_3H_2P_3O_{10}\cdot 1.5H_2O$.
(1) 3 hr grinding at the relative humidity of 40%
(2) 6 hr grinding at the relative humidity of 40%
(3) 3 hr grinding at low pressure
(4) 6 hr grinding at low pressure

that the crystal of NaH_2PO_4 is very stable for grinding or recrystallizes easily even if the lattice is disturbed.*[4] Although $Na_2H_2P_2O_7$ becomes orthophosphates by grinding in air, it also condenses to tri- and higher-polyphosphates simultaneously at low pressure. $Na_3H_2P_3O_{10}$ shows a tendency similar to $Na_2H_2P_2O_7$, namely, some tetra- and higher-polyphosphates are produced at low pressure.

From the above results, it is possible for the mechanism of (1) to take place. However, it is difficult to confirm the mechanism of (2) and this must be studied further in the future but the fact that the amounts of tetra- and higher-polyphosphates produced when $Na_3P_3O_9$ is ground at low pressure are much more than those produced by grinding $Na_2H_2P_2O_7$ and $Na_3H_2P_3O_{10}$ indicates the possibility of the mechanism of (2).

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*[4] Monosodium dihydrogen orthophosphate is ready to adhere to the mortar during grinding, and it may decrease the efficiency of grinding.