The Constitution of $NaPO_3$-Cr_2O_3 Melts

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Glassy and crystalline thermal products were made by heating a mixture of sodium metaphosphate glass and chromium(III) oxide with P/Cr ratios in the range from 1.0 to 300 at 1000 °C for 3 h in a platinum crucible and by then rapidly quenching the resulting melt. The crystalline substances were present in the products with P/Cr ratios smaller than 50 and were, except for chromium(III) oxide, an unknown substance and chromium(III) tripolyphosphate. The colorimetric determination and the measurement of the average chain length of polyphosphate anions present in the water-soluble parts of the products with P/Cr ratios larger than 50 showed that chromium(III) oxide reacts with sodium metaphosphate glass to make Cr–O–P linkages. Assuming that the glass has P–O–P, P–O$^-$, Cr–O–P, and Cr–O$^-$ linkages, a theoretical treatment of the degree of polymerization of condensed phosphates were made and compared with the data. It was concluded that the most reasonable chemical structure of the glassy thermal products of the $NaPO_3$–Cr_2O_3 system is $Cr(OP)_3$.

Several attempts to prepare condensed phosphates containing oxoacid anions of some elements other than phosphorus have been made. The investigated systems were arsenate–phosphates,[1] silicate–phosphates,[2] vanadate–phosphates,[3] and borate–phosphates.[4,5] It was reported that condensed compounds of this type have P–O–As, P–O–Si, P–O–V, and P–O–B linkages, respectively. The authors also have studied thermal products in antimonate–phosphate,[6–8] molybdate–phosphate,[9] tungstate–phosphate,[9] and aluminate–phosphate[10] systems. It was concluded that they have P–O–Sb, P–O–Mo, P–O–W, and P–O–Al linkages, respectively, and the most reasonable chemical structure of the glassy products is proposed.

In the present paper, glassy and crystalline substances of the $NaPO_3$–Cr_2O_3 system with various P/Cr ratios were prepared by heating a mixture of Graham's salt and chromium(III) oxide at 1000 °C for 3 h in order to obtain some information on the chemical composition and structure of the system. The compositions of condensed phosphates were determined by the paper-chromatographic analysis of their aqueous solutions. The identification of the crystalline products was made by X-ray diffractometry and the chemical structure of the glassy products was studied by the theoretical treatment of the degree of polymerization of the condensed phosphates contained in the glassy products.

Experimental

Materials and Procedure. Sodium metaphosphate glass was prepared by heating monosodium orthophosphate dihydrate in a platinum crucible at 1000 °C for 3 h and then by quenching the melt by placing the crucible in ice water. The chromium(III) oxide was of a commercial grade. A mixture of sodium metaphosphate glass and chromium(III) oxide with P/Cr ratios in the range from 1.0 to 300 was heated in a platinum crucible at 1000 °C for 3 h. The resulting product was quenched by the same method as that for the preparation of sodium metaphosphate.

Chromium(III) Pyro- and Tripolyphosphates. The X-ray diffraction data for chromium(III) orthophosphate are listed in the "A. S. T. M. Diffraction Data File," while those for chromium(III) pyro- and tripolyphosphates are not. Chromium(III) pyro- and tripolyphosphates were prepared by the following method for the purpose of referring the X-ray diffraction data for chromium(III) pyro- and tripolyphosphates with those for the thermal products. Chromium(III) pyro- and tripolyphosphates were made by adding chromium(III) nitrate to an aqueous solution of sodium pyro- and tripolyphosphates. The precipitate was filtered off and washed with water.[11] The hydrated compound was heated first at 500 °C for 1 h and then at 1000 °C for 1 h. The X-ray diffraction patterns of the dehydrated compounds were taken with a powder method. The determination of the chemical compositions of the compounds were made by paper-chromatographic analysis of the phosphates present in the precipitates and the quantitative analysis of chromium and phosphorus of the dehydrated compounds. The dehydrated compounds were insoluble in water. About one gram of these water-insoluble compounds was mixed completely with 10 g of potassium carbonate and then heated at 800 °C for 20 min in a platinum crucible. Chromium is oxidized to chromate and these water-insoluble compounds are converted to water-soluble compounds. The chromate and phosphate ions in the aqueous solution of the water-soluble compounds were determined by the colorimetric method of analysis;[12] for chromate, the diphenylcarbazide method was used and for phosphate the molybdenum blue method. In the case of the colorimetric analysis of phosphates, 2 ml of the Mo reagent and 1 ml of the reducing solution were used because this method is more suitable than that described in textbooks for the colorimetric analysis of the phosphates contained in water-soluble compounds. Accordingly, the colorimetric measurement of phosphorus must be made under the condition that the concentration of phosphorus is less than 10 γ/50 ml.

The crystalline thermal products of the $NaPO_3$–Cr_2O_3 system were also insoluble in water. The determination of chromium and phosphorus of the crystalline thermal products were made by using the same method as that for chromium(III) pyro- and tripolyphosphates. The quantitative analysis of the phosphates present in the water-soluble thermal products was made as follows.

Paper Chromatography and Colorimetric Determination of Phosphates in the Water-soluble Thermal Products. One-dimensional paper chromatography was used for the separation of the phosphate species contained in the water-soluble thermal products by using the solvents described in a previous paper.[10] About one gram of the product was placed in 50 ml of water and the mixture was stirred for one hour at room temperature. The insoluble part was then filtered off, dried, and weighed for

the purpose of measuring the solubility of the product. About 8 μl of the sample solution was placed on the starting point of Toyo No. 51A filter paper (2 by 50 cm) and developed for 40 h at 5 °C. The identifications and determinations of each phosphate spot on a chromatogram were carried out by using the same method as that described in a previous paper.[6]

The Measurement of the Average Chain Length of Phosphates in Glassy Thermal Products. The method used in a previous paper[6] was adopted for the measurement of the average chain length of polyphosphates contained in the thermal products. The measurement of the average chain length of polyphosphates was achieved for sample solutions of the thermal products with P/Cr ratios larger than 80 and no appreciable effect of chromium ions on the measurement of the average chain length of polyphosphates was observed.

X-Ray Diffractometry. The samples were ground to powder which could pass through a 150 mesh sieve. Their X-ray diffraction patterns were taken by using a powder method on a Toshiba X-ray diffractometer, ADG-102.

Infrared Spectral Measurement. The infrared spectra of the products were recorded on a JASCO infrared spectrophotometer, model IR-G, by using a KBr tablet method.

Results and Discussion

Chromium(III) Pyro- and Tripolyphosphates. The P/Cr ratios of the chromium(III) pyro- and tripolyphosphates obtained by adding chromium(III) nitrate to an aqueous sodium pyro- or tripolyphosphate solution were 1.5 and 1.8, respectively. The values of the P/Cr ratios correspond to the theoretical values of the P/Cr ratios of $Cr_4(P_2O_7)_3$ and $Cr_5(P_3O_{10})_3$. The X-ray diffraction diagrams of the dehydrated chromium(III) pyro- and tripolyphosphates are shown in Fig. 1.

Amount of the Water-soluble Parts in the Thermal Products and Identification of the Thermal Products by X-Ray Diffractometry. The thermal products with P/Cr ratios larger than 80 were amorphous, while those with P/Cr ratios in the range from 1.0 to 50 contained crystalline substances. The X-ray diffraction diagrams of the crystalline thermal products with P/Cr ratios in the range from 1.0 to 3.0 are shown in Fig. 1. The X-ray diffraction diagrams of the thermal products with P/Cr ratios of 1.0 and 2.0 contain peaks of chromium(III) oxide and an unknown crystalline substance. The peaks due to chromium(III) oxide and chromium(III) tripolyphosphate appear in the X-ray diffraction pattern of the thermal product with a P/Cr ratio of 3.0. The X-ray diffraction diagrams for the products with P/Cr ratios in the range from 5.0 to 50 were the same as that for chromium(III) tripolyphosphate and hence chromium(III) tripolyphosphate is the only crystalline substance contained in the thermal products with P/Cr ratios in the range from 5.0 to 50. Accordingly, it could be concluded that the P–O–P linkages of high-polyphosphate in this system are broken to make chromium(III) tripolyphosphate. It is noteworthy that chromium(III) oxide reacts with $NaPO_3$ glass to produce chromium(III) tripolyphosphate and not to make chromium(III) ortho- and pyrophosphates. The unknown crystalline substance and chromium(III) tripolyphosphate present in the thermal products were insoluble in water. The amount of water-soluble parts in the products are listed in Table 1. The results of identification of the crystalline products by X-ray diffractometry are also shown in Table 1.

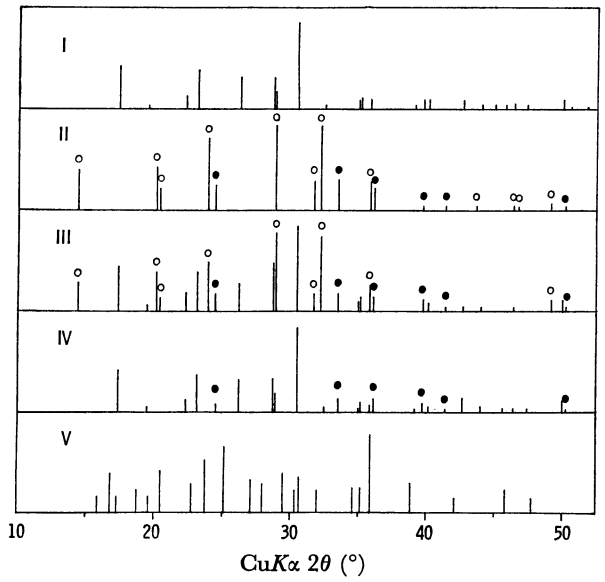


Fig. 1. X-Ray diffractograms of the thermal products, $Cr_4(P_2O_7)_3$, and $Cr_5(P_3O_{10})_3$.
I: $Cr_5(P_3O_{10})_3$, II: product with the P/Cr ratio of 1.0, III: product with the P/Cr ratio of 2.0, IV: product with the P/Cr ratio of 3.0, V: $Cr_4(P_2O_7)_3$.
○: Unknown peak for assignment, ●: peak attributable to Cr_2O_3 (Ref. ASTM card 6-504).

TABLE 1. AMOUNT OF WATER-SOLUBLE PARTS IN THE PRODUCTS AND IDENTIFICATION OF THE THERMAL PRODUCTS BY X-RAY DIFFRACTOMETRY

P/Cr	X-Ray diff.	Water-soluble parts (%)
1.0	Unknown, Cr_2O_3	5.7
2.0	Unknown, Cr_2O_3, $Cr_5(P_3O_{10})_3$	29
3.0	Cr_2O_3, $Cr_5(P_3O_{10})_3$	52
5.0—50	$Cr_5(P_3O_{10})_3$	67—98
80—300	Glassy	100

Unknown: unknown crystalline product (see Fig. 1).

Distribution of Phosphates. The results of quantitative analysis of the phosphates contained in the water-soluble parts of the thermal products are listed in Table 2. The contents of ortho-, pyro-, and tripoly-

TABLE 2. DISTRIBUTION OF PHOSPHATES OF WATER-SOLUBLE PARTS IN THE PRODUCTS

P/Cr	Ortho	Pyro	Tri	Tri-meta	Tetra-meta	Higher
1.0	3.0	11.1	33.1			52.8
2.0	1.0	4.1	17.0			77.9
3.0	1.1	2.5	11.2	1.3	0.8	83.1
5.0	0.8	1.7	6.2	1.2	0.8	89.3
7.0	0.5	0.8	3.1	2.0	1.5	92.1
10	0.7	0.6	1.0	3.0	1.4	93.3
15	0.4	0.5	0.7	3.3	1.3	93.8
20—300				2—4	1—3	93—97

phosphates decrease with an increase in the P/Cr ratio, while those of high-polyphosphates increase with an increase in the P/Cr ratio. This result is in good agreement with those of the other systems described in previous papers.[6-10] By the same considerations as in previous papers, it can reasonably be concluded that chromium(III) oxide reacts with sodium metaphosphate to make a Cr–O–P linkage at 1000 °C and that the Cr–O–P linkage of the water-soluble products is readily hydrolyzed to produce chromium and phosphate ions in water solutions. The contents of trimeta- and tetrametaphosphates do not change much with the variation in the P/Cr ratio and hence the formation of trimeta- and tetrametaphosphates may be little affected by chromium.

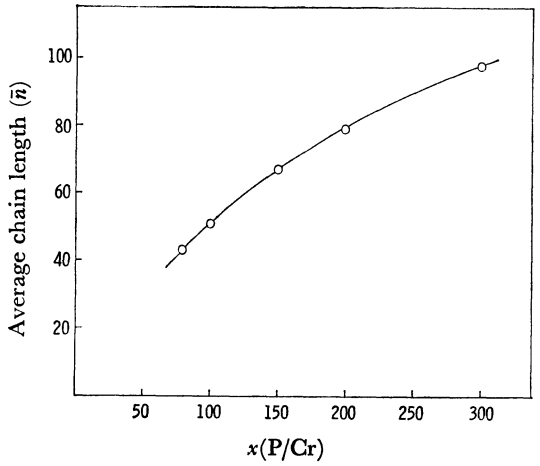
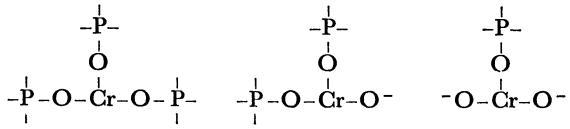


Fig. 2. Variation of average chain length of polyphosphates present in the thermal products with P/Cr ratios larger than 80.

Average Chain Length of Polyphosphates and the Chemical Structure of Glassy Products. The behavior of chromium contained in the glassy and water-soluble thermal products can be examined by measuring the correlation between the average chain length of polyphosphates and the P/Cr ratio of the products,[2,6-10] because the chain length of the polyphosphates present in the thermal products is affected by the coordination number of chromium. To obtain the correlation, it is necessary that the thermal product dissolves completely in water. Therefore, the average chain length of the polyphosphates present in the glassy products with P/Cr ratios larger than 80 was measured. The result is shown in Fig. 2 and indicates that the average chain length of the polyphosphates contained in the glassy products increases with an increase in the P/Cr ratio. This tendency is the same as that of the distribution of polyphosphates obtained by quantitative analysis. Accordingly, it can be concluded that this result is one proof of the presence of the Cr–O–P linkage in the glassy products. The correlation between the chromium coordination number and the average chain length of polyphosphates in the glassy products can be discussed theoretically employing the method described in previous papers.[2,6-10] Depending upon the method, the average chain length, $\bar{n}$, of the polyphosphates in the glass of the $NaPO_3$–Cr_2O_3 system is given by the following equation:

$$(\bar{n}+2)/\bar{n} = (x+y-z+fx)/x \quad (1)$$

where, x, y, and z are respectively the number of phosphorus atoms, P–O–Cr linkages, and Cr–O^- linkages per atom of chromium and where f is the factor shortening the chain length of the polyphosphates, given with respect to an atom of phosphorus. The previous results[2,6-10] indicate that the value of f is in the range from 0.01 to 0.025 under the conditions employed in this experiment. There are three possible structures containing P–O–Cr and Cr–O^- linkages, which are as follows:



Structure A Structure B Structure C

The average chain length of the polyphosphates present in the glassy products can be calculated on the basis of these chemical structures. The calculated values are listed in Table 3. When the f factor is 0.01, the calculated values of $\bar{n}$ based on Structure A are very close to the measured ones throughout the range of P/Cr ratios from 80 to 300. From these results, it may be reasonably concluded that the chemical structure of the glassy thermal products of the Cr_2O_3–$NaPO_3$ system with P/Cr ratios larger than 80 is the Structure A and hence the valence of chromium which contributes to the shortening of the chain length of polyphosphates is three. The chromium coordination number in the glassy products may be larger than three (in general, the coordination number of chromium is six or four). The coordination numbers which do not contribute to the shortening of the chain length of polyphsophates cannot be discussed by using the method described above. The P–O–Cr linkage which does not affect the average chain length of polyphosphates may be produced by the interaction between chromium and the oxygen atom of a P=O bond.

Table 3. Average chain length of polyphosphates of the $NaPO_3$–Cr_2O_3 system with P/Cr ratios larger than 80

x (P/Cr)	$\bar{n}$ Found	$\bar{n}$ calcd by Eq. 1 (f=0.01) Structure A (y=3, z=0)	B (y=2, z=1)	C (y=1, z=2)
80	43	42	89	—
100	51	50	100	∞
150	67	67	120	600
200	79	80	133	400
300	98	100	150	300

Infrared Spectra. The infrared spectra of sodium metaphosphate glass, chromium(III) oxide, chromium(III) tripolyphosphate, and the thermal products with P/Cr ratios in the range from 1.0 to 15 are shown in Fig. 3. Since the infrared spectra of the thermal products with P/Cr ratios larger than 20 are the same as that of sodium metaphosphate glass, the existence of the absorptions of the Cr–O–P linkage in the glassy products

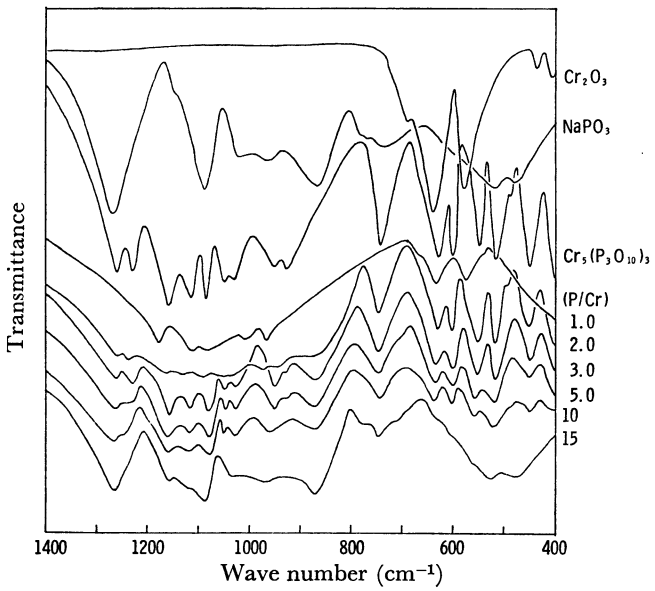


Fig. 3. IR spectra of Cr_2O_3, $NaPO_3$, $Cr_5(P_3O_{10})_3$, and the products with P/Cr ratios from 1.0 to 15.

cannot be discussed. The infrared spectrum of the thermal product with a P/Cr ratio of 1.0 contains the absorptions due to chromium(III) oxide (absorptions at 640 and 580 cm^{-1}) and does not contain an absorption due to chromium(III) tripolyphosphate, while the infrared spectra of the thermal products with P/Cr ratios larger than 2.0 exhibit an absorption attributable to chromium(III) tripolyphosphate. The absorption of chromium(III) tripolyphosphate becomes gradually ambiguous with an increase in the P/Cr ratio from 3.0 to 15. The infrared spectra of the water-insoluble parts which were obtained by treating with water the thermal products with P/Cr ratios of 5.0—50 are the same as that of chromium(III) tripolyphosphate. These results agree well with those obtained above.

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