Thermal Products in the System of $NaPO_3$ Glass-Al_2O_3

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The glassy and crystalline products were made by heating a mixture of aluminum oxide and sodium metaphosphate glass with P/Al ratios in the range from 1.0 to 300 at 1000 °C for 3 hr. The crystalline substance was present in the products with P/Al ratios smaller than 5.0 and was, except for aluminum oxide, always aluminum orthophosphate. The quantitative analysis and the measurement of the average chain length of the phosphates contained in the soluble parts of the products showed that aluminum oxide reacts with sodium metaphosphate to make Al–O–P linkages. A theoretical treatment of the average chain length of the polyphosphates present in the aluminate-phosphates was also made. By comparing the calculated average chain length with the measured one, it has been concluded that the most reasonable chemical structure of the glassy products of the aluminate-phosphates is $Al(OP)_3$. By the analysis of the infrared spectra of the thermal products, four-way branching points may be said to exist in the glassy products.

From the viewpoint of pure chemistry, the thermal products of arsenate-phosphates,[1] silicate-phosphates,[2] vanadate-phosphates,[3] and borate-phosphates[4,5] have been studied in to obtain some information on the reactivity between these oxo-acid salts at a moderately high temperature and on the chemical structures of the products. By analyzing the hydrolysis products, it has been revealed that there is a P–O–As, P–O–Si, P–O–V, or P–O–B linkage in each of the products. The authors also studied antimonate–phosphates,[6–8] molybdate–phosphates,[9] and tungstate–phosphates;[9] it has been concluded that they have a P–O–Sb, P–O–Mo, or P–O–W linkage respectively. The most reasonable chemical structure of the glassy products has also been reported.

It is well known that aluminum ions react with orthophosphoric acid to form an aggregation polymer, which have three-dimensional networks, in water.[10] In aluminate-phosphates or borate-phosphates, the presence of a four-way branching point was pointed out by Van Wazer.[11] In the present paper, the thermal products of the $NaPO_3$–Al_2O_3 system have been made in an attempt to obtain some information on the structure of the products in connection with the information mentioned above.

Experimental

Materials and Procedure. All the materials used other than sodium metaphosphate were of a commercial grade. The sodium metaphosphate was made by heating monosodium orthophosphate in a platinum crucible at 1000 °C for 3 hr and by then quenching the melt by placing the crucible in ice water. A mixture of sodium metaphosphate and α-aluminum oxide with P/Al ratios in the range from 1.0 to 300 was heated in a platinum crucible at 1000 °C for 3 hr; the resulting product was quenched by the method used in the preparation of sodium metaphosphate.

Paper Chromatography. One-dimensional paper chromatography was used for the separation of phosphate species contained in the products by using acidic and basic solvents. The compositions of the solvents are listed in Table 1. The acidic solvent was used for the separation of ortho-, pyro-, tri-, and long-chain phosphates, while the basic solvent was used for the separation of trimeta- and tetrametaphosphates. About one gram of the product was placed in 50 ml of water, and then the mixture was stirred for one hour at room temperature. The insoluble parts were then filtered off, dried, and weighed for the measurement of the solubility of the product. About 5 μl of the sample solution was spotted on a filter paper of Toyo No. 51A (2 by 50 cm) and developed for 40 hr at 5 °C. After the filter paper had then been dried at 75 °C for more than 30 min, a perchloric acid-molybdate solution was sprayed on the paper. The paper was dried again and exposed to ultraviolet rays until blue spots appeared. The identification of each spot on the chromatogram was made by comparing the spots with those of known phosphates.

TABLE 1. COMPOSITION OF THE SOLVENTS USED FOR THE PAPER CHROMATOGRAPHY

Acidic solvent	Isopropyl alcohol	70 ml
	25% aqueous trichloroacetic acid	20 ml
	Water	10 ml
	28% aqueous ammonia	0.3 ml
Basic solvent	Isopropyl alcohol	38.7 ml
	Isobutyl alcohol	20 ml
	Water	40 ml
	28% aqueous ammonia	0.5 ml

Colorimetric Determination of Phosphates. The determination of the phosphates on a chromatogram was carried out by the colorimetric method described in a previous paper.[6]

The Measurement of the Average Chain Length of Polyphosphates. The method used in our previous paper[6] was adopted for the measurement of the average chain length of polyphosphates contained in the thermal products, but since aluminum ions present in the sample solution strongly affected the pH titration of the solution, the aluminum ions were previously removed by the oxine method.[12]

X-Ray Diffractometry. The samples were ground with an agate mortar until they could pass through a 150 mesh sieve. Their X-ray diffraction patterns were taken by means of a powder method using 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 the KBr tablet method.

Results and Discussion

Solubility and Identification of Crystalline Products by X-Ray Diffractometry. The results of the measurement of the solubility of the products and of the identification of the crystalline products by X-ray diffractometry are listed in Table 2. The identification was carried out by comparing the X-ray diffraction peaks of the products with those on ASTM cards. All the X-ray peaks of the products were due to aluminum oxide and/or aluminum orthophosphate. According to the above results, it could be concluded that the P–O–P linkages of high polyphosphate in this system are broken to make aluminum orthophsophate at 1000 °C. The insoluble parts in the products with the P/Al ratios in the range from 7.0 to 15 were amorphous.

TABLE 2. AMOUNT OF WATER-SOLUBLE PARTS OF THE PRODUCTS AND IDENTIFICATION OF THE CRYSTALLINE PRODUCTS BY X-RAY DIFFRACTOMETRY

P/Al	X-Ray diff.	Water-soluble parts (%)
1.0	Al_2O_3, $AlPO_4$	3.1
2.0	Al_2O_3, $AlPO_4$	3.6
2.5	$AlPO_4$	13
3.0	$AlPO_4$	29
5.0	$AlPO_4$	67
7.0	glassy	87
10	glassy	98
15	glassy	99
20—300	glassy	100

TABLE 3. DISTRIBUTION OF PHOSPHATES OF WATER-SOLUBLE PARTS IN THE PRODUCTS

P/Al	Phosphate (P%)					
	Ortho	Pyro	Tri	Tri-meta	Tetra-meta	Higher
1.0	100					
2.0	100					
2.5	100					
3.0	100					
5.0	98.0	2.0				
7.0	11.0	17.9				71.1
10	3.8	2.3	10.5	1.3	1.5	80.6
15	2.9	2.0	3.8	3.3	2.1	85.9
20	2.7	2.4	2.1	2.9	2.4	87.5
30	1.9	1.8	1.8	3.4	2.6	88.5
50	1.4	0.3	0.7	4.5	4.2	88.9
80	0.5	0.3	1.0	2.8	2.1	93.3
100				3.5	2.3	94.2
150				2.6	2.5	94.9
200				2.8	3.1	94.1
300				3.0	2.9	94.1

Distribution of Phosphates. The results of the colorimetric determination of phosphates in the soluble parts of the products are shown in Table 3. The contents of ortho-, pyro-, and tripolyphosphates decrease with an increase in the P/Al ratio, while those of high-polyphosphates increase with an increase in the P/Al ratio. This tendency is the same as that reported in previous papers.[1–4,6–9] By analogy with the previous papers, it can reasonably be concluded that sodium metaphosphate reacts with aluminum oxide to make an Al–O–P linkage at 1000 °C and that the Al–O–P linkage of the water-soluble products is readily hydrolyzed in a water solution. Since the contents of trimeta- and tetrametaphosphates so not change much with the variation in the P/Al ratio, the formation of the metaphosphates may be little affected by aluminum.

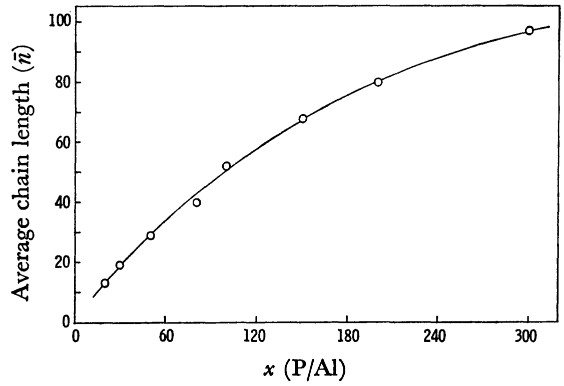

Fig. 1. Variation of average chain length of polyphosphates present in the products with P/Al ratios larger than 20

Average Chain Length of Polyphosphates and the Chemical Structure of Glassy Products. In aluminate-phosphates, the coordination number of aluminum can be four. The behavior of aluminum in the glassy products studied in the present paper can be examined by measuring the correlation between the average chain length of polyphosphates and the P/Al ratio. To obtain the correlation, it is necessary that the thermal product is dissolved completely in water. Therefore, the average chain length of the polyphosphates present in the glassy products with P/Al ratios larger than 20 were measured; the results are shown in Fig. 1. It may clearly be seen that the average chain length of the polyphosphates contained in the glassy products increases with an increase in the P/Al ratio. This tendency is the same as that found in the colorimetric determination of phosphates. The correlation between the coordination number of aluminum and the average chain length of polyphosphates in the thermal products can be considered theoretically by the method described in previous papers.[2,6–9] According to the theory, the relation between the P/Al ratio and the average chain length of polyphosphates can be written as follows:

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

where $\bar{n}$ is the average chain length of polyphosphates, where x, y, and z are, respectively, the number of phosphorus atoms, P–O–Al linkages, and Al–O^- linkages per atom of aluminum, and where f is the factor shortening the chain length of the polyphosphates, given with respect to an atom of phosphorus. It is known by previous experiments[2,6–9] that the value of f is in the range from 0.01 to 0.025 under the conditions employed in this experiment. The bonding formulas

TABLE 4. CHEMICAL STRUCTURES OF THE GLASSY PRODUCTS WITH P/Al RATIOS LARGER THAN 20

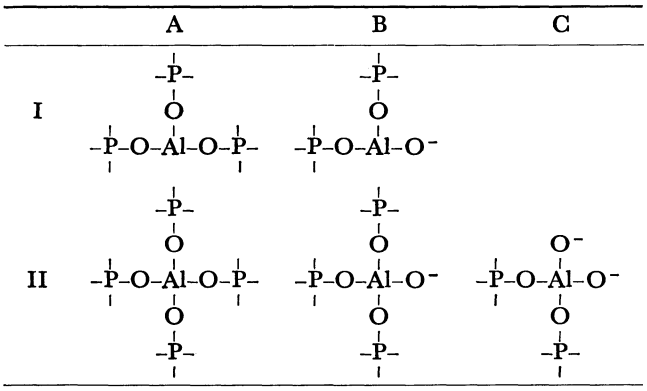

TABLE 5. AVERAGE CHAIN LENGTH OF POLYPHOSPHATES OF THE $NaPO_3$–Al_2O_3 SYSTEM WITH P/Al RATIOS LARGER THAN 20

x (P/Al)	$\bar{n}$ Found	$\bar{n}$ calcd. by Eq. (1) (f=0.01) Model[a)] IA	IB	IIA	IIB	IIC
20	13	13	33	10	18	200
30	19	18	46	14	26	200
50	29	29	67	22	40	200
80	40	42	89	33	57	200
100	52	50	100	40	67	200
150	68	67	120	55	86	200
200	80	80	133	67	100	200
300	97	100	150	86	120	200

a) The models refer to Table 4.

of aluminum with phosphates in glassy products are shown in Table 4. Other structures could be described for the system, but it can readily be seen in the following discussion that the other structures are unreasonable for the system. The calculated values of $\bar{n}$ based on the chemical structures in Table 4 are listed in Table 5. As may clearly be seen in the table, when the f factor is 0.01, the calculated values of $\bar{n}$ based on the IA structure in Table 4 are very close to the measured ones throughout the range of P/Al ratios from 20 to 300. From these results, it may reasonably be concluded that the chemical structure of the glasses of the Al_2O_3–$NaPO_3$ system with P/Al ratios larger than 20 is the IA structure in Table 4. This also means that the valence of aluminum, which contributes to the shortening of the chain length of polyphosphates, is three.

Infrared Spectra. The infrared spectra of sodium metaphosphate glass and the glassy products with P/Al ratios of 3.0, 5.0, and 7.0 are shown in Fig. 2. Since the infrared spectra of the glassy products with P/Al ratios larger than 7.0 are the same as that of sodium metaphosphate, the existence of the absorption of the Al–O–P linkages in the glassy products with P/Al ratios larger than 20 can not be discussed. According to Corbridge and Lowe,[13)] the absorption of 1270 cm^{-1} in the spectrum of sodium metaphosphate may be

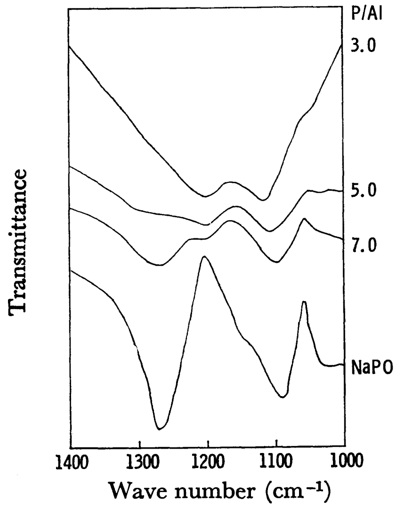

Fig. 2. IR spectra of the products with P/Al ratios from 3.0 to 7.0 and $NaPO_3$ glass

considered to be due to P=O stretching. When the P/Al ratio decreases from 7.0 to lower values, this absorption shifts to lower wave numbers in the spectra of the products. It can be concluded that the bonding force of the P=O bond decreases with a decrease in the P/Al ratio. This phenomenon can be explained as a P=O bond transfers to the P⋯O⋯Al bond by the coordination of aluminum. By extending this result to the glassy products with P/Al ratios larger than 10, it can be said that four-way branching points may exist in the glassy products.

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10) For example, J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. 1, Interscience Publishers, New York (1958), p. 558.
11) J. R. Van Wazer, *ibid.*, p. 422.
12) For example, Nippon Bunseki Kagakukai, "Bunseki Kagaku Binran," Maruzen, Tokyo (1971), p. 156. In the course of this analysis, it is necessary to heat an acidic sample solution (the pH is near 3) at 70 °C; this causes the scission of the P–O–P linkages. Therefore, the period of heating the sample solution was as short as possible (about 3 min.), and aging was done at room temperature for about 20 min.
13) D. E. C. Corbridge and E. J. Lowe, *J. Chem. Soc.*, **1954**, 493 and 4555.