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The Chemical Structures of Glasses of the $NaPO_3$-Sb_2O_3-Na_2O System

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Glassy and crystalline substances of the $NaPO_3$-Sb_2O_3-Na_2O system with P/Sb ratios in the range from 1.0 to 300 were prepared by heating $NaPO_3$, Sb_2O_3, and Na_2CO_3 at 1000°C and by then quenching the melts of the mixtures. Samples with P/Sb ratios smaller than 5.0 were obtained as crystalline substances containing amorphous substances. The chemical compositions of these crystalline substances were estimated from the data obtained by X-ray diffractometry and paper chromatography. Samples with P/Sb ratios larger than 7.0 were obtained as glassy substances. Condensed phosphates were separated by paper-chromatographic analysis, and the average degree of the polymerization of the phosphates was measured by the pH-titration method. It has been found that the crystalline substances in the samples with P/Sb ratios in the range from 1.0 to 5.0 were Sb_2O_5, $NaSbO_3$, and an unknown crystalline substance. Assuming that the glasses have the P-O-P, P-O^-, P-O-Sb, and Sb-O^- linkages, a theoretical treatment of the degree of polymerization of condensed phosphates has been made and compared with the experimental data. It has been concluded that the glasses with P/Sb ratios larger than 7.0 have P-O-P, P-O^-, and P-O-Sb linkages.

Several attempts to prepare condensed phosphates containing oxoacid anions of some elements other than phosphorus have been made. For instance, Thilo and his co-workers investigated arsenate-phosphates,[1] and Ohashi and his co-workers investigated phosphate-silicates,[2] vanadate-phosphates,[3] and borate-phosphates.[4] It has been reported that the condensed compounds of this type have P-O-As, P-O-Si, P-O-V, and P-O-B linkages respectively. All of these oxoacid anions have a tendency to polymerize at a high temperature.

In the present work, glassy and crystalline substances of sodium phosphate-antimonates with various P/Sb ratios have been prepared in order to obtain some information on the chemical compositions and structures of the system. The compositions of the condensed phosphates have been determined by paper-chromatographic analysis of their aqueous solutions, while the structures of the crystals have been estimated by means of a study of their X-ray diffraction patterns. The theoretical treatment of the degree of polymerization of the condensed phosphates has been made and compared with the experimental data. The results reveal that the glasses also have P-O-Sb linkages.

Experimental

Materials. Sodium metaphosphate was prepared by heating monosodium dihydrogen orthophosphate dihydrate in a platinum crucible at 1000°C for 3 hr and by then quenching the melt by pressing it between two stainless steel plates. The average chain length of the glass thus obtained was about 100. The antimony trioxide and sodium carbonate were commercial reagents.

Glassy Substances. After the weight of the glass had been measured, calculated amounts of antimony trioxide and of sodium carbonate were taken on the glass and then mixed in an alumina mortar. The number of moles of sodium carbonate was equal to that of antimony trioxide. The mixture of these three materials was melted at 1000°C for 2 hr and then quenched by the method used in the preparation of sodium metaphosphate. By this procedure, glassy substances of the $NaPO_3$-Sb_2O_3-Na_2O system with P/Sb ratios in the range from 7.0—300 were prepared. All the glasses thus obtained were transparent and colourless.

1) K-H. Jost, H. Worzala, and E. Thilo, *Z. Anorg. Allg. Chem.*, **325**, 98 (1963).
2) S. Ohashi and F. Oshima, This Bulletin, **36**, 1489 (1963).
3) S. Ohashi and T. Matsumura, *ibid.*, **35**, 501 (1962).
4) T. Nakamura and S. Ohashi, *ibid.*, **40**, 110 (1967).

Crystalline Substances. A mixture of sodium metaphosphate, antimony trioxide, and sodium carbonate (with P/Sb ratios of 1.0, 2.0, and 5.0) was heated in a platinum crucible at 1000°C for 2 hr, and then the melts were quenched by placing the crucible in ice water. The crystalline substances with P/Sb ratios of 1.0 and 2.0 were opaque and a weak yellow, and the substances with a P/Sb ratio of 5.0 were transparent and colourless.

Paper Chromatography. The glassy substances were dissolved in water, and the phosphate species in the solution were separated by paper chromatography and then determined colorimetrically. Acidic and basic solvents were used for the paper chromatography. The acidic solvent was made by mixing 70 m*l* of ethyl alcohol, 5 g of trichloroacetic acid, 0.3 m*l* of concentrated aqueous ammonia, and 30 m*l* of water, it was used for the separation of ortho-, di-, tri-, tetra-, and long-chain phosphates. The basic solvent was made by mixing 40 m*l* of isopropyl alcohol, 20 m*l* of isobutyl alcohol, 1 m*l* of concentrated aqueous ammonia, and 39 m*l* of water, it was used for the separation of trimeta- and tetrametaphosphates. A sample solution was made by dissolving 1—2 g of the crystalline or the glassy substance in 150 m*l* of water. About 5 μl of the sample solution was placed on a filter paper of Toyo No. 53 of 2 by 40 cm and developed at room temperature for 20 hr. After the paper had been dried at 75°C for more than 30 min, it was sprayed a perchloric acid-molybdate solution so as to convert the phosphates into molybdophosphates. After it had then been dried again, the paper was exposed to ultraviolet light in order to reduce the molybdophosphates to blue complexes. Each band of the phosphates on the filter paper was identified by the same treatment of the reference solution of known phosphates.

The separated phosphates on the paper chromatograms were determined as follows, the filter paper containing each separated phosphates was cut at the demarcation line, and then immersed in 10 m*l* of a 0.1N aqueous solution of ammonia in a 50-m*l* Erlenmeyer flask. After 1 hr or more, this solution was transferred into a 25-m*l* volumetric flask, and then 10 m*l* of water and 2 m*l* of Lucena-Conde and Prat's reagent[5] were added. The flask was placed in a boiling-water bath for 1 hr, then cooled rapidly by placing it in a bath of cold water, and diluted to the mark with water. The absorbance of the solution was measured with a Shimadzu photoelectric photometer, Spectonic-20, at 800 mμ. The distribution of the phosphate species was calculated from the absorbance data.

The Measurement of the Average Chain Length of Polyphosphates. The average chain length of polyphosphates was measured by the pH-titration method proposed by Van Wazer, Griffith, and McCulough.[6,7] About 2 g of the glassy substance was dissolved in about 100 m*l* of water in a 250-m*l* Erlenmeyer flask. Most of the antimonate in the sample was precipitated and then filtered off. A twenty-five milliliters aliquot of the filtrate was diluted to about 100 m*l* and acidified with 1N hydrochloric acid to about pH 3 and then titrated with 0.1N sodium hydroxide. The volume of the 0.1N sodium hydroxide solution consumed between two inflection points, located at approximately pH 4.5 and 9.5, was measured. Twenty-five milliliters of another aliquot of the filtrate was transferred into a 250-m*l* Erlenmeyer flask, the mixture was diluted to about 80 m*l* with water, and then 10 m*l* of concentrated hydrochloric acid and 1 g of potassium chloride were added. The solution was boiled to dryness in order to hydrolyze completely all the condensed phosphates, the residue was dissolved with 50 m*l* of water and adjusted the pH to about 3 with a 6N carbonate-free sodium hydroxide solution. The solution was titrated by the same method mentioned above. If the volume of the 0.1N sodium hydroxide solution for the first titration is A, and if the volume for the second one is A_h, the average chain length, $\bar{n}$, is given by the $\bar{n}=2A_h/A$ equation, assuming that the only phosphates present in the glass are polyphosphates.

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

Results and Discussion

The ignition loss of the mixture of these three materials was equal to the weight of the CO_2 gas which evolved upon the decomposition of Na_2CO_3. After heating, therefore, the crystalline and the glassy substances formed the $NaPO_3$-Sb_2O_3-Na_2O system. According to the observation of these samples under a polarizing microscope, the samples with the P/Sb ratios of 1.0, 2.0, and 5.0 were composed of an opaque and a transparent portion, and the amounts of the opaque portion decreased when the P/Sb ratio increased. The glasses with P/Sb ratios larger than 5.0 were almost entirely composed of the transparent portion, and the crystalline substances were negligibly small. The crystalline substances in the samples with P/Sb ratios of 1.0, 2.0, and 5.0 can be estimated from the data obtained by X-ray diffractometry. The data for the $NaPO_3$-Sb_2O_3-Na_2O system, with P/Sb ratios of 1.0, 2.0, and 5.0, are given in Table 1. By means of the X-ray diffraction patterns

Table 1. Chemical compositions of substances of the $NaPO_3$-Sb_2O_3-Na_2O system with P/Sb ratios of 1.0—5.0

	X-Ray diffractometry			Paper chromatography Phosphate(P%)			
P/Sb	Sb_2O_5	$NaSbO_3$	Unknown	Ortho	Pyro	Tri	Tri-meta	High poly
1.0	##	##	+	46.5	32.1	1.3		20.1
2.0	#	#	##	41.9	24.2	1.8		32.1
5.0	—	—	+	6.1	34.7	18.2	7.7	33.3

of the samples with P/Sb ratios of 1.0, 2.0, and 5.0, it has been found that there are unknown peaks of a strong intensity at spacings of 7.40 Å and of a medium intensity at spacings of 6.21 Å. Other crystalline substances of the samples with P/Sb ratios of 1.0 and 2.0 are antimony pentoxide and sodium metaantimonate. The antimony pentoxide and sodium metaantimonate were identified by comparing the X-ray patterns of the samples with those of "A. S. T. M. Diffraction Data File." The X-ray diffraction patterns of no phosphate species appear. The antimony pentoxide and sodium metaantimonate contents in these samples decrease with the increase in the P/Sb ratio, while that of the unknown crystalline substance increases with the increase in the P/Sb ratio

5) F. Lucena-Conde and L. Prat, *Anal. Chim. Acta*, **16**, 473 (1957).

6) J. R. Van Wazer, E. J. Griffith, and J. F. McCulough, *Anal. Chem.*, **26**, 1755 (1954).

7) E. J. Griffith, *ibid.*, **28**, 525 (1956).

from 1.0 to 2.0. The crystalline substance of the sample with the P/Sb ratio of 5.0 consists only of the unknown substance, and the contents of the unknown substance are small. From the results of the paper-chromatographic analysis of the samples with P/Sb ratios of 1.0, 2.0, and 5.0, it is found that the quantities of ortho- and pyrophosphate in the samples with the P/Sb ratios of 1.0 and 2.0 are very large, but those of the orthophosphate in the samples decrease rapidly with the increase in the P/Sb ratio from 2.0 to 5.0. When the samples are treated with water, white crystalline substances are deposited. In the X-ray diffraction patterns of the white deposits, there are also unknown peaks of a strong intensity at spacings of 7.40 Å and of a medium intensity at spacings of 6.41 Å, and the peaks of antimony trioxide, antimony pentoxide, and sodium metaantimonate. From these results, it may be concluded that the unknown crystalline substance is not dissolved in water and that all the sodium phosphate species contained in the samples compose an amorphous phase.

TABLE 2. DISTRIBUTION AND AVERAGE CHAIN LENGTH OF PHOSPHATES OF THE $NaPO_3$-Sb_2O_3-Na_2O SYSTEM WITH P/Sb RATIOS OF 7.0—300

	Phosphate (P%)						
P/Sb	Ortho	Pyro	Tri	Tri-meta	Tetra-meta	Higher	$\bar{n}$
7.0	2.7	28.8	21.6	5.4	8.5	33.1	3.6
10	2.0	15.8	7.2	5.6	7.9	61.5	4.7
15	2.0	8.5	7.4	5.6	6.4	70.1	7.0
20	1.9	5.2	5.2	5.0	5.4	77.2	8.4
30	1.8	4.4	4.2	4.3	4.3	80.9	11
50	1.5	4.0	3.9	3.8	4.4	82.3	21
80	1.1	3.3	3.5	3.3	4.1	84.7	29
100	0.8	2.4	3.0	2.6	3.7	87.5	37
150	0.6	1.3	2.5	2.0	3.3	90.3	49
200	0.4	0.9	1.0	1.5	3.4	92.8	52
300	0.4	0.7	0.8	0.8	2.9	94.4	65

When the samples of the glassy substances with the P/Sb ratios larger than 7.0 are treated with water, antimony trioxides are deposited. The compositions of the phosphate species in the sample solutions were determined by paper chromatography. The results for the samples are given in Table 2. When the P/Sb ratio increases, the contents of ortho- and pyrophosphate decrease, and that of high polyphosphate increases. The contents of tripolyphosphate increase with the increase in the P/Sb ratio from 1.0 to 7.0 and decrease with the decrease in the P/Sb ratio from 7.0 to 300. The trimetaphosphate contents indicate the largest value when the P/Sb ratio is 5.0, and decrease with the increase in the P/Sb ratio. The tetrametaphosphate contents decrease with the increase in the P/Sb ratio from 7.0 to 300.

The average chain lengths of the polyphosphates given in Table 2 were measured by the pH titration method, assuming that the phosphates were composed of polyphosphates and did not contain ortho- and ring phosphates. By the results of the paper-chromatographic analysis of the glasses, it is shown that the quantities of orthophosphate and of ring phosphates are less than several per cent. Therefore, the effect of their presence on the calculation of the average chain length of polyphosphates is disregarded in the following discussion.

Between the Na/P ratio and the average chain length, $\bar{n}$, of sodium polyphosphate, there is this relation:

$$\mathrm{Na/P} = (\bar{n}+2)/\bar{n} \qquad (1)$$

where Na/P is the atomic ratio of these two elements. If antimony trioxide does not react with phosphate glass to form P-O-Sb linkages in the melted state, the Na/P ratio is equal to $(x+1)/x$, where x is the P/Sb ratio. By using these relations, Eq. (2) is obtained:

$$\bar{n} = 2x \qquad (2)$$

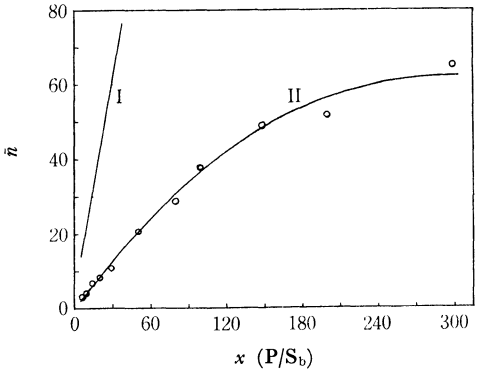
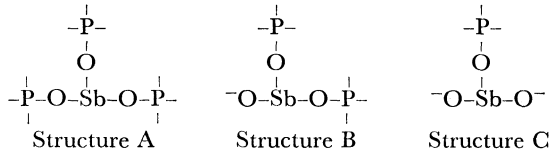


Fig. 1. Variation of average chain length of polyphosphates.
I: Values calculated by Eq. (2)
II: Experimental values

The straight line, I, in Fig. 1 indicates this relation. Curve II in Fig. 1 indicates the relation between the measured average chain length of polyphosphates and the P/Sb ratio, x. The great discrepancy between the straight line, I, and the curve, II, means that the above assumption is not correct. Therefore, the sodium phosphate glass seems to react with antimony trioxide at a high temperature to form P-O-Sb linkages. There are three possible structures containing P-O-Sb and Sb-O$^-$ linkages. Assuming that the hydrolytic scission



of P–O–Sb linkage occurs rapidly in water, the average chain length, $\bar{n}$, of the polyphosphates in the glass of the $NaPO_3$–Sb_2O_3–Na_2O system is given by Eq. (3):

$$(\bar{n}+2)/\bar{n} = (x+y+1-z)/x \qquad (3)$$

where x, y, and z are the numbers of phosphorus atoms, P-O-Sb linkages, and Sb-O$^-$ linkages per atom of antimony. If the glasses are composed only of Structure A, y is 3 and z is 0, and x is the P/Sb ratio of the glass. The average chain length of the polyphosphate can be calculated by inserting these values into Eq. (3). The calculated values of $\bar{n}$ are given in Table 3. The

Table 3. Average chain length of polyphosphates

x (P/Sb)	$\bar{n}$ Found	Column I $\bar{n}$ calcd by Eq. (3) Structure A ($y=3$, $z=0$)	Structure B ($y=2$, $z=1$)	Structure C ($y=1$, $z=2$)	Column II $\bar{n}$ calcd by Eq. (4) ($f=0.02$) Structure A ($y=3$, $z=0$)	Structure B ($y=2$, $z=1$)	Structure C ($y=1$, $z=2$)
7.0	3.6	3.5	7.0	∞	3.4	6.5	100
10	4.7	5.0	10	∞	4.8	9.1	100
15	7.0	7.5	15	∞	7.0	13	100
20	8.4	10	20	∞	9.1	17	100
30	11	15	30	∞	13	23	100
50	21	25	50	∞	20	33	100
80	29	40	80	∞	29	44	100
100	37	50	100	∞	33	50	100
150	49	75	150	∞	43	60	100
200	52	100	200	∞	50	67	100
300	65	150	300	∞	60	75	100

underlined values are the average chain length nearest to the measured one. As the column I of Table 3 shows, even the calculated values of the average chain length based on Structure A are considerably larger than the measured values when x is larger than 20.0. The presence of a branching point and impurities in the phosphate-antimonate glasses shortens the chain length of polyphosphates. Representing all these factors by factor f, Eq. (3) is modified into Eq. (4):

$$(\bar{n}+2)/\bar{n} = (x+y+1-z+fx)/x \qquad (4)$$

where f is given with respect to an atom of phosphorus. If f is arbitrarily set at 0.02, the calculated average chain lengths of the glasses shown in column II of Table 3 are given by Eq. (4). If the factor, f, is zero, Eq. (4) is reduced to Eq. (3). As column II of Table 3 shows, the values calculated on the basis of Structure A are close to the experimental values through out the range of P/Sb ratios from 7.0 to 300. According to above discussion, it seems reasonable to conclude that the structural framework of the glasses of condensed phosphate-antimonates is composed of Structure A, and that Structure B and C are not involved in the structural framework.

Summary

Crystalline and glassy substances of phosphate-antimonate systems with P/Sb ratios in the range from 1.0 to 300 were prepared by heating a mixture of sodium metaphosphate, antimony trioxide, and sodium carbonate at 1000°C for 2 hr. The samples with P/Sb ratios in the range from 1.0 to 5.0 were obtained as crystalline substances containing amorphous substances, while those with P/Sb ratios in the range from 7.0 to 300 were obtained as glassy substances. By paper chromatography and X-ray diffractometry, the samples containing crystalline and amorphous substances were found to be composed of Sb_2O_5, $NaSbO_3$, an unknown crystalline substance, and various condensed phosphates. From the results of paper chromatography and the measurement of the average chain length of the phosphates by the pH titration method, it was revealed that the higher the P/Sb ratio, the longer were the chains of the polyphosphates produced; it was concluded that the $NaPO_3$-Sb_2O_3-Na_2O glasses with the P/Sb ratios in the range from 7.0 to 300 had P-O-Sb linkages.