The Chemical Structure of Glass of the $NaPO_3$–Sb_2O_4 System

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Glassy substances of the $NaPO_3$–Sb_2O_4 system with P/Sb ratios in the range from 5.0 to 300 were prepared by heating a mixture of $NaPO_3$ glass and Sb_2O_4 at 1000 °C and by then rapidly quenching the melt of the mixture. From the results of the colorimetric determination and the average degree of polymerization of the condensed phosphates, it has been found that the chain length of the phosphates increases with an increase in the P/Sb ratio. When the glass was treated with water, antimony trioxide was deposited. By using these results, a theoretical treatment for the average degree of polymerization of condensed phosphates has been made and it has been concluded that there are P–O–Sb linkages in the glass of the $NaPO_3$–Sb_2O_4 system.

Phosphate glasses containing oxoacid anions of some elements other than phosphorus have attracted the interest of many investigators. In our previous papers,[1,2] we reported the chemical structure of sodium phosphate glass containing antimony tri- or pentoxide. In the present paper, we will examine the structural framework of sodium phosphate glass containing antimony tetroxide by using the same method as in the previous papers.

Experimental

Materials and Procedure. Sodium phosphate glass was prepared by heating monosodium orthophosphate in a platinum crucible at 1000 °C for 3 hr and by then quenching the resulting melt by placing the crucible in ice water. Antimony tetroxide was made by heating antimony trioxide at 800 °C until a constant weight was reached. The increase in the mass was very close to the calculated value of the oxidation of antimony trioxide to tetroxide (98.3%). Glassy products were obtained by heating mixture of the $NaPO_3$–Sb_2O_4 system with P/Sb ratios in the range from 5.0 to 300 in a platinum crucible at 1000 °C for 2 hr and by then quenching the melts rapidly by placing the crucible in ice water. The distribution and the average degree of the polymerization of phosphate species contained in the glasses were measured by using the same method as in the previous papers.[1,2]

Results and Discussion

The ignition loss of a mixture of the $NaPO_3$–Sb_2O_4 system was very close to the calculated value of the reduction of antimony tetroxide to trioxide. When the glassy substances were treated with an alkaline solution, a white substance was deposited; the deposit gave only X-ray diffraction patterns of antimony trioxide. It can be concluded from the results that the valence of antimony in the glasses may be three. The glassy substances are colorless and transparent, and give no X-ray diffraction patterns. The phosphates present in the aqueous solution of the glassy products were separated by paper chromatography and were then determined colorimetrically. As Table 1 shows, the quantities of ortho-, pyro-, and triphosphates decrease with an increase in the P/Sb ratio, while those of higher polyphosphates increase. The quantities of tri- and tetrametaphosphates are very small throughout the full range of P/Sb ratios.

Table 1. Distribution of phosphates of the $NaPO_3$–Sb_2O_4 system with P/Sb ratios of 5.0—300

P/Sb	Phosphate (P%)					
	Ortho	Pyro	Tri	Trimeta	Tetrameta	Higher
5.0	10.6	34.2	10.5	3.7	2.9	38.1
7.0	9.9	15.0	7.7	3.1	3.0	61.3
10	2.1	7.0	5.3	4.9	2.4	78.3
15	1.5	6.4	3.4	3.5	3.8	81.4
20	1.3	5.5	3.3	4.0	3.1	82.8
30	1.3	5.2	3.3	3.6	1.6	85.0
50	1.0	4.1	2.1	4.7	1.7	86.4
80	1.1	1.8	2.9	4.0	1.2	89.0
100	0.9	1.2	2.8	4.0	2.7	88.4
150				3.6	3.7	92.7
200				2.9	3.3	93.8
300				2.8	1.2	96.0

The average degree of polymerization of $NaPO_3$ glass was about 100, while that of the phosphates contained in the glassy products, which was also measured by the pH titration method increases with an increase in the P/Sb ratio, as may clearly be seen in Fig. 1, it can be concluded that sodium phosphate glass may react with antimony oxide to form the P–O–Sb linkage and the valence of the antimony may be reduced to three under these conditions. The

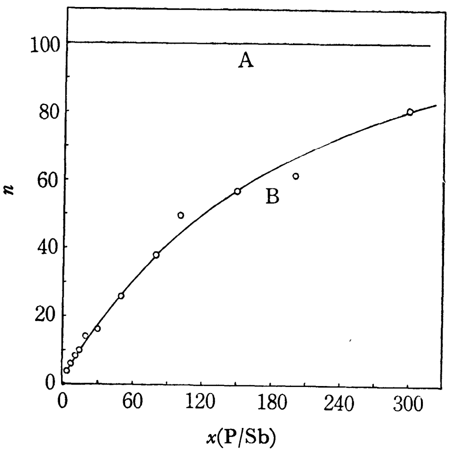


Fig. 1. Variation of average chain length of polyphosphates.
A: Sodium phosphate glass
B: Experimental values of the $NaPO_3$–Sb_2O_4 system

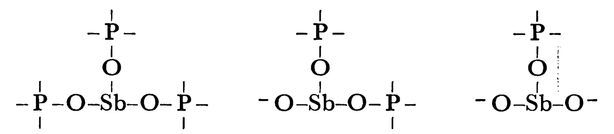
1) M. Watanabe, K. Tanabe, T. Takahara, and T. Yamada, This Bulletin, **44**, 712 (1971).
2) M. Watanabe and M. Kato, *ibid.*, **45**, 1058 (1972).

P–O–Sb linkage may be very much less stable than the P–O–P linkage. Therefore, the P–O–Sb linkage may be rapidly hydrolyzed to produce phosphate ions and antimony trioxide in an aqueous solution.

By using these results as a basis, a theoretical treatment for the average degree of polymerization of the phosphates present in the glassy products can be made. The theory has already been described in previous papers.[1,2] A summary of the theory is as follows. The valence of antimony present in the glasses is considered to be three, and there are three possible types of structures containing P–O–Sb linkages. If x, y, and z are the numbers of phosphorus atoms, P–O–Sb linkages, and $Sb–O^-$ linkages per atom of antimony respectively, the average chain length, $\bar{n}$, of the polyphosphates produced by the hydrolysis of P–O–Sb linkages is given by Eq. (1):

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

The values calculated by using this equation are listed in Column I of Table 2. When x is larger than 30,



Structure A Structure B Structure C

even the calculated values of $\bar{n}$ based on Structure A are larger than the measured ones. Considering other factors which shorten the chain length of the phosphates present in the glasses, for example, the branching points and impurities, Eq. (1) is modified into Eq. (2):

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

where f is the factor shortening the chain length of the polyphosphate and is given with respect to an atom of phosphorus. As may clearly be seen in Column II of Table 2, when the f factor is arbitrarily set at 0.015, the calculated values of $\bar{n}$ based on Structure A are very close to the measured ones throughout the range of P/Sb ratios from 5.0 to 300. From these results, it may reasonably be concluded that the structural framework of the glasses of the $NaPO_3$–Sb_2O_4 system with P/Sb ratios larger than 5.0 is Structure A.

TABLE 2. AVERAGE CHAIN LENGTH OF POLYPHOSPHATES OF THE $NaPO_3$–Sb_2O_4 SYSTEM

		Column I $\bar{n}$ calcd by Eq. (1) Structure			Column II $\bar{n}$ calcd by Eq. (2) (f=0.015) Structure		
x (P/Sb)	$\bar{n}$ Found	A (y=3, z=0)	B (y=2, z=1)	C (y=1, z=2)	A (y=3, z=0)	B (y=2, z=1)	C (y=1, z=2)
5.0	4.1	3.3	10	—	3.3	9.3	—
7.0	5.8	4.7	14	—	4.5	13	—
10	8.8	6.7	20	—	6.3	17	—
15	9.7	10	30	—	9.3	25	—
20	14	13	40	—	12	31	—
30	16	20	60	—	17	41	—
50	26	33	100	—	27	57	∞
80	38	53	160	—	38	73	800
100	50	67	200	—	45	80	400
150	57	100	300	—	57	92	240
200	62	133	400	—	67	100	200
300	81	200	600	—	80	109	171

According to the results described in this paper and in the previous papers,[1,2] when the P/Sb ratio is larger than 5.0, antimony tetr- and pentoxides are reduced to trioxide and the trioxide reacts with $NaPO_3$ glass to form Structure A at 1000 °C. The values of the f factors of the $NaPO_3$–Sb_2O_3 and –Sb_2O_5 systems were 0.02 and 0.01 respectively. The difference in the value of the factor between these systems may be caused by the quantities of impurities contained in the antimony oxides and/or the experimental conditions—for example, the cooling speed of the melts. The f factor of the pure sodium phosphate glass ranges from 0.025 to 0.01, depending on the conditions of the preparation.