The Chemical Structures of Glasses of the $NaPO_3$-Sb_2O_3 and $NaPO_3$-Sb_2O_5 Systems

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(Received May 12, 1971)

Glassy substances of the $NaPO_3$-Sb_2O_3 and $NaPO_3$-Sb_2O_5 systems with P/Sb ratios in the range from 5.0 to 300 were prepared by heating $NaPO_3$ and Sb_2O_3, or Sb_2O_5 at 1000°C, and by then quenching the melts of the mixtures. The condensed phosphates were separated by paper-chromatographic analysis and determined colorimetrically, and the average degree of polymerization of the phosphates was measured by the pH-titration method. From these results, it has been found that the degree of polymerization of the phosphates increased with the increase in the P/Sb ratio. When the glassy samples of both the systems were treated with water, antimony trioxide was deposited. The results show that, in the glassy samples of both the systems, the valency of antimony is three, 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 of both the systems with P/Sb ratios larger than 5.0 have P–O–P, P–O$^-$, and P–O–Sb linkages.

Condensed phosphates containing oxoacid anions of some elements other than phosphorus have been prepared by several investigators.[1–4] In a previous paper,[5] the chemical compositions and structures of glasses of the $NaPO_3$-Sb_2O_3-Na_2O system were reported. It has been revealed in these papers that, in structures of condensed phosphates containing oxoacid anions of an element, X, other than phosphorus, there are P–O–X linkages. In the present work, glassy substances of the $NaPO_3$-Sb_2O_3 and $NaPO_3$-Sb_2O_5 systems were prepared in order to obtain some information on the chemical compositions and the structural framework of the systems. As for the glasses of the $NaPO_3$-Sb_2O_3 system, it has been presupposed that its structural framework is the same as that of the glasses of the $NaPO_3$-Sb_2O_3-Na_2O system, this has been confirmed by the measurement of the degree of polymerization and by a theoretical treatment of that of the condensed phosphates. The theoretical treatment of the degree of polymerization of the condensed phosphates revealed that the glasses of these two systems have P–O–Sb linkages. The compositions of the condensed phosphates have been determined by the paper-chromatographic analysis of their aqueous solutions.

Experimental

Materials. Monosodium dihydrogen orthophosphate dihydrate was heated in a platinum crucible at 1000°C for 3 hr and then converted to a glass of sodium metaphosphate by cooling a melt in a crucible. The average chain length of the glass thus obtained was about 100. The antiomony trioxide and pentoxide were commercial reagents.

Classy substances. A mixture of sodium metaphosphate and antimony trioxide, or pentoxide was melted in a platinum crucible at 1000°C for 2 hr and then quenched by placing the crucible in ice water. By this procedure, glasses of the $NaPO_3$-Sb_2O_3 and $NaPO_3$-Sb_2O_5 systems with P/Sb ratios of 5.0 to 300 were prepared. All the glasses thus obtained were transparent and colorless.

Paper Chromatography. The phosphate species in the solution of the glassy substances were separated by paper chromatography and then determined colorimetrically. Except for the acidic solvent, the procedure was the same as that described in a previous paper.[5] In this experiment, the acidic solvent was made by mixing 26.5 m*l* of water, 0.25 m*l* of concentrated aqueous ammonia, 5 g of trichloroacetic acid, and 73.5 m*l* of isopropyl alcohol. It was used for the separation of ortho-, di-, tri-, tetra-, and long-chain phosphates.

The Measurement of the Average Chain Length of Polyphosphates. The average degree of the polymerization of phosphate species in the glassy samples was also measured by the method described in the previous paper.[5]

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 with nickel-filtered CuKα radiation, by using a Toshiba X-ray diffractometer, ADG-102.

Results and Discussion

The samples with P/Sb ratios larger than 5.0 were completely transparent and opaque. The data of X-ray diffractometry of these samples indicated that they were amorphous. The chemical compositions of the phosphate species contained in the glassy substances were estimated by paper-chromatographic analysis. The data of the paper chromatography for the $NaPO_3$-Sb_2O_3 system with P/Sb ratios of 5.0 to 300 are given in Table 1, while those for the $NaPO_3$-Sb_2O_5 system with P/Sb ratios of 5.0 to 300 are given in Table 2. It is found that the ortho-, pyro-, and tripolyphosphate contents of both the systems decrease with the increase in the P/Sb ratio from 5.0 to 300. The quantities of trimeta- and tetrametaphosphate are less than several percent throughout the range of P/Sb ratios from 5.0 to 300. The quantities of high polyphosphate increase with the increase in the P/Sb ratio.

When the glassy samples of the $NaPO_3$-Sb_2O_3 and $NaPO_3$-Sb_2O_5 systems were treated with a 0.03 N sodium hydroxide solution, a white substance was deposited. A study of the X-ray diffraction patterns

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TABLE 1. DISTRIBUTION OF PHOSPHATES OF THE $NaPO_3$-Sb_2O_3 SYSTEM WITH P/Sb RATIOS OF 5.0-300

	Phosphate (P%)					
P/Sb	Ortho	Pyro	Tri	Tri-meta	Tetra-meta	Higher
5.0	10.2	20.5	17.7	1.6	2.9	47.1
7.0	4.1	16.7	16.1	2.8	5.2	55.1
10	3.9	11.7	11.7	2.9	2.4	67.4
15	1.8	10.3	11.0	2.9	3.6	70.4
20	2.3	8.5	6.9	5.2	4.0	73.1
30	2.4	4.8	9.7	3.5	3.4	76.2
50	2.2	2.2	4.3	3.9	4.6	82.8
80	0.5	1.6	2.9	3.6	4.9	86.5
100		1.5	2.6	4.4	3.1	88.4
150		1.3	1.9	2.7	4.1	90.0
200		1.9	1.7	3.0	3.1	90.3
300		1.7	1.6	3.4	2.9	90.4

TABLE 2. DISTRIBUTION OF PHOSPHATES OF THE $NaPO_3$-Sb_2O_5 SYSTEM WITH P/Sb RATIOS OF 5.0—300

	Phosphate (P%)					
P/Sb	Ortho	Pyro	Tri	Tri-meta	Tetra-meta	Higher
5.0	16.0	18.1	14.6	6.6	4.0	40.7
8.0	14.1	14.0	6.8	5.1	4.0	56.0
10	5.4	6.6	6.5	3.9	3.7	73.9
15	4.5	4.2	3.0	2.5	3.5	82.3
20	5.1	3.9	2.8	3.2	2.5	82.5
30	3.7	2.9	2.1	2.9	2.2	86.2
50	1.6	2.5	2.8	2.9	2.7	87.5
80	1.0	1.6	2.0	3.5	1.9	90.0
100	0.5	1.5	1.2	3.5	2.4	90.9
150	0.9	1.3	0.5	3.3	2.8	91.2
200				2.5	2.2	95.3
300				1.9	1.4	96.7

of the deposit showed it to be antimony trioxide. This indicates that the antimony pentoxide contained in the samples of the $NaPO_3$-Sb_2O_5 system is reduced to antimony trioxide. The careful treatment of weight change of this system supports the reduction. Therefore, the valency of antimony in the glassy samples of both the systems is three.

The average chain length of the polyphosphates contained in the samples of both the systems was measured. The results of the paper chromatography of these glasses show that the quantities of orthophosphate and of ring phosphates are not very large, therefore, the effect of their presence on the calculation of the average chain length of polyphosphates is disregarded in the following discussion. It is well known that the average chain length, $\bar{n}$, of polyphosphates in a sodium phosphate glass is given by the $Na/P=(\bar{n}+2)/\bar{n}$ equation, where Na/P is the atomic ratio of both the elements. If antimony trioxide or pentoxide does not react with phosphate glass to form P–O–Sb linkages in the melted state, the average chain length of phosphates in the glassy samples does not change when the P/Sb ratio is changed. The straight line,

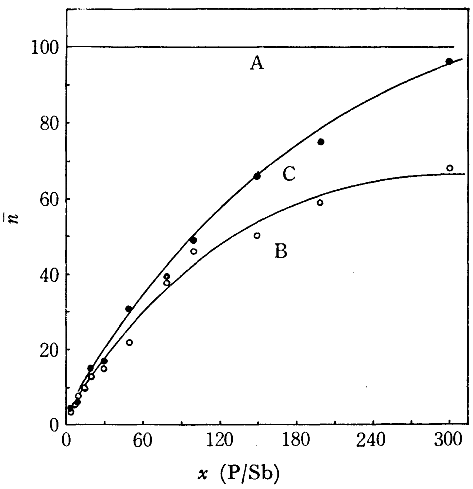
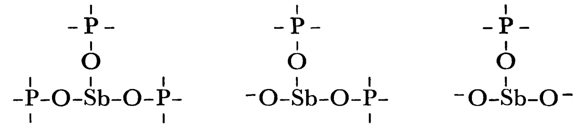


Fig. 1. Variation of average chain length of polyphosphates.
A: Pure sodium metaphosphate
B: Experimental values of the $NaPO_3$-Sb_2O_3 system
C: Experimental values of the $NaPO_3$-Sb_2O_5 system

A, in Fig. 1 exhibits this relation. Curves B and C in Fig. 1 indicate the relation between the measured average chain length of polyphosphates and the P/Sb ratio, x, of the $NaPO_3$-Sb_2O_3 and $NaPO_3$-Sb_2O_5 systems respectively. The great discrepancy between the straight line, A, and the curves B and C, and the results of paper chromatography indicate that the phosphate glass reacts with antimony trioxide or pentoxide at a high temperature to form P–O–Sb linkages.



Structure A Structure B Structure C

From the finding that, when the glassy samples of both the systems are treated with a 0.03 N sodium hydroxide solution, antimony trioxide is deposited, it may be concluded that there are three possible types of structures containing P–O–Sb and $Sb–O^-$ linkages. The average chain length, $\bar{n}$, of the polyphosphates produced by the hydrolytic scission of P–O–Sb linkages in the glassy samples of both the systems is given by Eq. (1):

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

where x, y, and z are the numbers of phosphorus atoms, P–O–Sb linkages, and $Sb–O^-$ linkages per atom of antimony respectively. For Structure A, B, or C, y is 3, 2, or 1, and z is 0, 1, or 2, respectively. The average chain length of polyphosphates derived from the $NaPO_3$-Sb_2O_3 and $NaPO_3$-Sb_2O_5 systems with various P/Sb ratios, x, was calculated by inserting these values into Eq. (1). The calculated values of $\bar{n}$ are given in Tables 3 and 4. The underlined values are the average chain length nearest to the measured one. As is shown by Column I of Table 3 or 4, 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 30 or 80 respectively. Other factors that shorten the chain length of the polyphosphates present in the phosphate-antimonate

TABLE 3. AVERAGE CHAIN LENGTH OF POLYPHOSPHATES OF THE $NaPO_3$-Sb_2O_3 SYSTEM

		Column I $\bar{n}$ calcd by Eq. (1)			Column II $\bar{n}$ calcd by Eq. (2) (f=0.02)		
		Structure			Structure		
x	$\bar{n}$	A	B	C	A	B	C
(P/Sb)	Found	(y=3, z=0)	(y=2, z=1)	(y=1, z=2)	(y=3, z=0)	(y=2, z=1)	(y=1, z=2)
5.0	3.5	3.3	10	—	3.2	9.1	—
7.0	5.4	4.7	14	—	4.5	12	—
10	7.4	6.7	20	—	6.3	17	—
15	10	10	30	—	9.1	23	—
20	13	13	40	—	12	29	—
30	15	20	60	—	17	38	—
50	22	33	100	—	25	50	∞
80	38	53	160	—	35	62	267
100	46	67	200	—	40	67	200
150	50	100	300	—	50	75	150
200	59	133	400	—	57	80	133
300	68	200	600	—	67	86	120

TABLE 4. AVERAGE CHAIN LENGTH OF POLYPHOSPHATES OF THE $NaPO_3$-Sb_2O_5 SYSTEM

		Column I $\bar{n}$ calcd by Eq. (1)			Column II $\bar{n}$ calcd by Eq. (2) (f=0.01)		
		Structure			Structure		
x	$\bar{n}$	A	B	C	A	B	C
(P/Sb)	Found	(y=3, z=0)	(y=2, z=1)	(y=1, z=2)	(y=3, z=0)	(y=2, z=1)	(y=1, z=2)
5.0	4.3	3.3	10	—	3.3	9.5	—
8.0	5.9	5.3	16	—	5.2	15	—
10	7.2	6.7	20	—	6.5	18	—
15	10	10	30	—	9.5	26	—
20	15	13	40	—	13	33	—
30	17	20	60	—	18	46	—
50	31	33	100	—	29	67	—
80	39	53	160	—	42	89	—
100	49	67	200	—	50	100	∞
150	66	100	300	—	67	120	600
200	75	133	400	—	80	133	400
300	96	200	600	—	100	150	300

glasses are the existence of a branching point and impurities. If all these factors are represented by the factor, f, Eq. (1) is modified into Eq. (2):

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

where f is given with respect to an atom of phosphorus. The f factor is arbitrarily set at 0.02 for the $NaPO_3$-Sb_2O_3 system and at 0.01 for the $NaPO_3$-Sb_2O_5 system. The value of f of $NaPO_3$-Sb_2O_3 system is identical with that of the $NaPO_3$-Sb_2O_3-Na_2O system. The average chain lengths shown in Column II of Tables 3 and 4 are obtained by inserting these values into Eq. (2). The average chain length of pure sodium metaphosphate is usually in the range from 80 to 200, depending on the conditions of preparation. The f factor of the pure sodium phosphate glass is given by $(\bar{n}+2)/\bar{n}=(1+f)/1$; it ranges from 0.025 to 0.01. Therefore, the f factor of 0.02 for the $NaPO_3$-Sb_2O_3 system and that of 0.01 for the $NaPO_3$-Sb_2O_5 system seem to be reasonable. As is shown in Column II of Tables 3 and 4, the average chain lengths, as calculated on the basis of Structure A, are very close to the experimental values throughout the range of P/Sb ratios from 5.0 to 300. In view of the above discussion, it may reasonably be concluded that the structural framework of the glasses of the $NaPO_3$-Sb_2O_3 and $NaPO_3$-Sb_2O_5 systems with P/Sb ratios in the range from 5.0 to 300 was composed of Structure A, and that Structures B and C were not involved in the structural framework.