CONTRIBUTION FROM THE
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The Constitution of Rubidium Phosphate Glasses

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Extensive paper chromatographic investigations have been carried out in this Laboratory on the constitution of condensed phosphates, particularly, strong phosphoric acids,[1] sodium acid phosphate glasses,[2] sodium, potassium, lithium phosphate glasses,[3,4] and mixed alkali phosphate glasses.[5,6] These condensed phosphates are found to contain polyphosphate anions, linear as well as cyclic; the distribution of total phosphorus among the various polymers, hereafter merely called distribution, is found to be a function of cation/phosphorus ratio. The results[4] obtained in this Laboratory for the alkali phosphate glasses agree in general but differ in detail from the data predicted by the polymer theory of Van Wazer[7] and Parks and Van Wazer.[8]

The constitution[9] of rubidium phosphate glasses, with $\bar{n}$, the number-average chain length,[10] varying from 3 to 9, now has been determined.

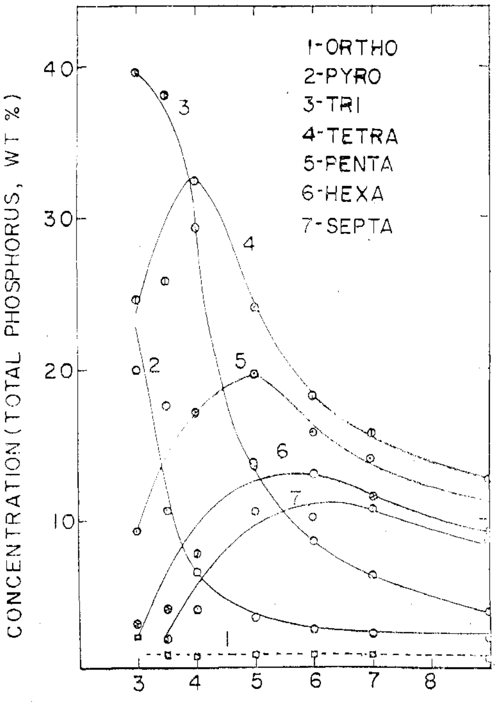

Fig. 1.—Constitution of rubidium phosphate glasses.

Experimental

The starting materials were rubidium carbonate (Rb_2CO_3) and ammonium dihydrogen phosphate ($NH_4H_2PO_4$), both of Fisher certified reagent quality. The calculated amounts of the starting materials were mixed in a platinum crucible and melted over a Meker burner for about 30 min. and the melt was quenched by dipping the crucible in water. By this procedure it was possible to obtain glasses from compositions with $\bar{n}$ equal to or higher than 3.5; the composition with an $\bar{n}$ value of 3, however, devitrified when so prepared. A glass of this composition was made in a synchronized copper block–cooled strip furnace,[11] in which very rapid cooling (less than about 1/100 of a second) could be obtained. All the glasses were hygroscopic, and the hygroscopicity increased with increase in the rubidium content of the glass. The glasses dissolved readily in water. The water solutions of the glasses were analyzed for the distribution of total phosphorus among the various polyphosphate anions, by the paper chromatographic methods developed in this Laboratory and described in detail earlier.[12]

Results and Discussion

In Fig. 1 the weight % distribution of total phosphorus among the various phosphate anion groups is plotted against $\bar{n}$. The results of the chromatographic analyses on the basis of which the above figure is plotted are given in Table I.

The data are the average values of duplicates; in general, the difference was not greater than 0.5, and in most cases it was much less. It

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(1) A. L. Huhti and P. A. Gartaganis, *Can. J. Chem.*, **34**, 785 (1956).

(2) A. E. R. Westman, M. J. Smith, and P. A. Gartaganis, *ibid.*, **37**, 1764 (1959).

(3) A. E. R. Westman and J. P. Crowther, *J. Am. Ceram. Soc.*, **37**, 420 (1954).

(4) A. E. R. Westman and P. A. Gartaganis, *ibid.*, **40**, 293 (1957).

(5) M. Krishna Murthy, M. J. Smith, and A. E. R. Westman, *ibid.*, **44**, 97 (1961).

(6) A. E. R. Westman and M. Krishna Murthy, *ibid.*, **44**, 475 (1961).

(7) J. R. Van Wazer, *J. Am. Chem. Soc.*, **72**, 644 (1950).

(8) J. R. Parks and J. R. Van Wazer, *ibid.*, **81**, 1023 (1959).

(9) In the glass literature, one normally encounters the term "structure" by which is meant a knowledge of the relative positions of all the atoms making up the glass and of the forces acting between them. The term "constitution" has been adopted for this discussion because in this investigation the writers separated molecular groupings or "constituents" present in a glass and studied them without regard to their original geometrical arrangement in glass.

(10) $\bar{n}$, the number-average chain length, represents the average chain length of the linear polymers and is given by the equation $\bar{n} = 2/(M/P - 1)$, where M/P is the over-all cation/phosphorus ratio of such polymers.

(11) The method consists of heating a small amount of the material on a platinum strip by a low-voltage high-amp. current and quenching the melt by two copper blocks. A detailed description of the method will be published in *J. Am. Ceram. Soc.*

(12) M. J. Smith, *Anal. Chem.*, **31**, 1023 (1959).

TABLE I

THE CONSTITUTION OF RUBIDIUM PHOSPHATE GLASSES

Distribution of Phosphorus in Wt. %

Number-av. chain length, $\bar{n}$	3	3.5	4	5	6	7	9
Phosphate fraction							
Ortho-	2.2	0.9	0.7	0.8	0.7	0.8	0.7
Pyro-	19.9	17.6	6.5	3.4	2.7	2.4	2.1
Tri-	39.6	38.1	29.4	13.7	8.4	6.2	3.9
Tetra-	24.6	25.8	32.5	24.1	18.2	15.8	12.6
Penta-	9.3	10.5	17.2	19.7	15.9	14.1	9.1
Hexa-	3.1	4.1	7.7	13.5	13.0	11.4	8.5
Septa-	...	2.1	4.0	10.5	10.2	10.7	9.0
Hf and HP[a]	1.3	0.9	2.0	14.3	30.9	38.6	54.1
			No. of molecules per 100 phosphorus atoms				
Theor.	33.3	28.6	25.0	20.0	16.7	14.3	11.1
Exptl.	31.9	31.1	26.7	21.2	18.4	16.7	14.2

[a] "Hf and HP" indicate high-fractions and hypoly. "Hypoly" is a term adopted in this Laboratory for polyphosphates containing more than nine phosphorus atoms per chain. The term "Hf" includes the fractions between chain-length nine and the last fraction that could be clearly separated in chromatographic analyses.

should be pointed out, however, that in the case of glass with $\bar{n}$ equal to 3, although duplicates for any one preparation agreed well, there were rather wide variations between different preparations; these glasses were very difficult to prepare and were very hygroscopic. In view of the fact that consistently good results were obtained for glasses with $\bar{n}$ values equal to or higher than 3.5, it is believed that the over-all picture of the constitution presented in Fig. 1 is correct.

As regards the ortho fraction, it is observed that it is of the order of 1% in all the glasses studied. Hence, it is to be considered as a hydrolysis product of the chain phosphates and not as a true constituent of glass. Cyclic phosphates were not determined; nevertheless, since in previous investigations on lithium, sodium, and potassium phosphate glasses of comparable compositions the values were of the order of 2 to 3%, it is believed that this will not affect our conclusions materially.

A comparison of the distribution curves ob-

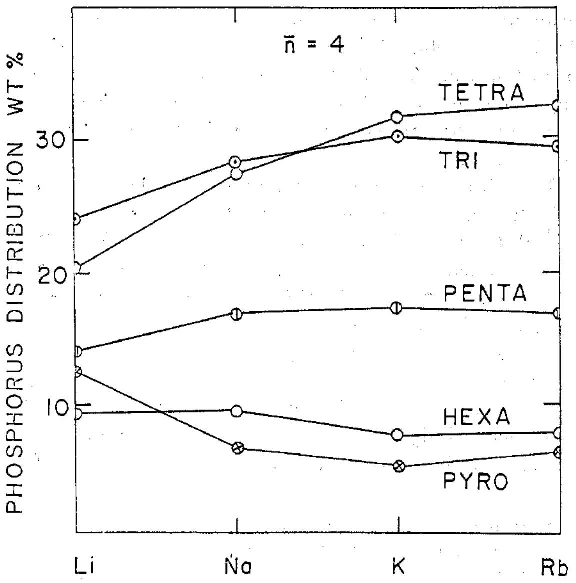

Fig. 2.—Influence of cation on the constitution of alkali phosphate glasses with $\bar{n}$ = 4.

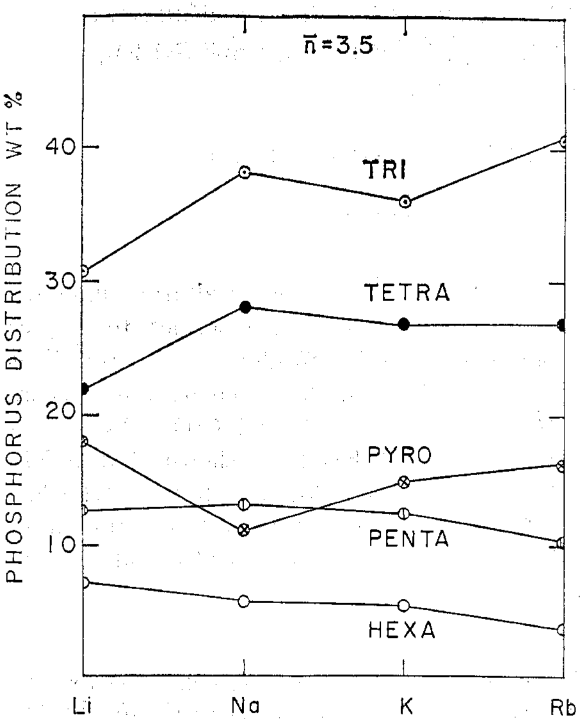

Fig. 3.—Influence of cation on the constitution of alkali phosphate glasses with $\bar{n}$ = 3.5.

tained for rubidium phosphate glasses with those for lithium, sodium, and potassium phosphate glasses shows that they are essentially similar; there are, nevertheless, slight but systematic differences. Thus, for example, in glasses with an $\bar{n}$ value of 4, it is observed that as the size of the alkali ion increases (Li^+ = 0.60 Å., Na^+ = 0.95 Å., K^+ = 1.33 Å., and Rb^+ = 1.48 Å.) the pyro- and hexapolyphosphates gradually decrease whereas tri-, tetra-, and pentapolyphosphates gradually increase (Fig. 2). At $\bar{n}$ values of 5 or higher similar trends exist except that pyro- and tripolyphosphates decrease whereas the others increase to some extent. At $\bar{n} = 3.5$ the changes are not systematic, as shown in Fig. 3.

According to the polymer theory of condensed phosphates, as presently developed, only the ratio cation/phosphorus decides the distribution of phosphorus among the various polymeric anion units. The results of this investigation point out that the effect of monovalent cations cannot be completely ignored in developing the polymer theory.

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Preparation of the Fluorosulfonates: $KI(SO_3F)_4$, $KBr(SO_3F)_4$, $SnCl(SO_3F)_3$, and $CrO_2(SO_3F)_2$

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It is known that peroxydisulfuryl difluoride, $S_2O_6F_2$, reacts with some chlorides to replace chlorine by the fluorosulfonate group.[1] This type of reaction now has been used to prepare $SnCl(SO_3F)_3$ from $SnCl_4$ and $CrO_2(SO_3F)_2$ from CrO_2Cl_2. It also has been shown that $S_2O_6F_2$ fails to replace the halogen in KBr or KI when reacting at about room temperature. Instead of this the complex salts, $KBr(SO_3F)_4$ and $KI(SO_3F)_4$, are formed.

Experimental

Materials.—Peroxydisulfuryl difluoride was prepared by the method of Dudley, *et al.*, by passing a stream of SO_3 containing a slight excess of F_2 through a "catalytic" reactor[1,2] (containing copper ribbon coated with silver fluoride(s)) at 165° using dry nitrogen as a carrier. The product was purified by pumping away fluorine fluorosulfonate and other volatile impurities while the material was held at −78°.[1] The potassium halogenides were of analytical quality. Stannic chloride and chromyl chloride were purified by vacuum distillation.

Potassium Tetrakis(fluorosulfonato)iodate(III).—An excess of peroxydisulfuryl difluoride was distilled into a weighed, cold bulb containing 0.271 mmole of KI. The bulb then was allowed to warm. A mildly exothermic reaction, evidenced by a slight warming of the reaction bulb, began to occur just below room temperature. At first the solid became brown in color. After several hours, however, it became white. The excess reagent was distilled out of the bulb, and the weight of the product was that of 0.267 mmole of $KI(SO_3F)_4$.

When a solution of sodium hydroxide was added, the product reacted according to the equation

$$3KI(SO_3F)_4 + 12OH^- \longrightarrow 2IO_3^- + 3K^+ + I^- + 12SO_3F^- + 6H_2O$$

rapidly and exothermically. Further hydrolysis of the fluorosulfonate to sulfate and fluoride ions took place by prolonged heating. The iodate was determined by iodometry using the "dead stop" potentiometric method.[3] The sulfate was determined as barium sulfate and the fluoride as triphenyltin fluoride.[4] *Anal.* Calcd.: iodate, 0.182 mmole; sulfate and fluoride, 1.08 mmoles. Found: iodate, 0.184 mmole; sulfate, 1.13 mmoles; fluoride, 1.09 mmoles.

Potassium tetrakis(fluorosulfonato)iodate(III) is a white solid which melts at 167–168° with slight decomposition yielding a green material which may be ISO_3F.[5] This salt does not react with F_2 at 100°.

Potassium Tetrakis(fluorosulfonato)bromate(III).—This salt was prepared in the same way as potassium tetrakis(fluorosulfonato)iodate(III) except that the reaction flask was closed by a break-seal rather than a stopcock. As the reactants warmed a chemical change started at about 0°. At first the solid became orange in color; then it slowly turned white. The flask was heated to 50° for several days to ensure complete reaction. KBr (4.697 mmoles) yielded a solid residue having the weight of 4.628 mmoles of $KBr(SO_3F)_4$.

The salt reacted with sodium hydroxide solution yielding oxygen and some bromine, the latter being quickly absorbed by the solution. The salt also produced some oxygen when it reacted with a solution containing a large excess of potassium iodide. In both cases the quantity of oxygen produced varied from one run to another. The solution from the alkaline hydrolysis was made acidic and then treated with $NaHSO_3$ to reduce BrO_3^- to Br^-. The sulfur dioxide then was removed by prolonged boiling. Bromide ion was determined as AgBr, sulfate as $BaSO_4$, and fluoride as triphenyltin

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