Condensed Vanadate-Phosphates

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It is well known that the structural frameworks of condensed phosphates are composed of P–O–P linkages. Some attempts to prepare condensed phosphates containing anions other than phosphate have been made. Thilo and his coworkers[1] have succeeded in making glasses and crystals of sodium or potassium arsenate-phosphates, which are composed of P–O–P and P–O–As linkages. Some experiments have been made on glasses of sulfate-phosphates[2] and silicate-phosphates[3]. The purpose of the present investigation is to prepare glasses and crystals of sodium vanadate-phosphates, which have P–O–V linkages.

Both the glasses and the crystals of alkali arsenate-phosphates, when dissolved in water, decompose by the scission of P–O–As linkages to give arsenate and mixtures of condensed phosphates[1]. As is the case with alkali arsenate-phosphates, sodium vanadate-phosphates, it is assumed, decompose by the scission of P–O–V linkages, when dissolved in water, to give vanadate and mixtures of condensed phosphates.

The present authors have made glasses and crystals of sodium vanadate-phosphates with various P/V ratios and have also obtained some information on the structures of the glasses and the crystals from paper chromatographic analyses of their aqueous solutions.

In the course of the present investigation it was found that vanadium(V) is partially reduced to vanadium(IV) when the starting materials, i.e., sodium metaphosphate, vanadium(V) oxide and sodium carbonate, are melted together to form the glasses or the crystals. Munakata et al.[4] found that a considerable amount of low valency vanadium, probably vanadium(IV), is produced when glasses of the V_2O_5-P_2O_5-BaO system are prepared.

Experimental

Vanadium(V) Oxide.—Ammonium metavanadate was recrystallized at least twice from its hot aqueous solution by adding ammonium chloride. The purified ammonium metavanadate was converted to vanadium(V) oxide by heating it at 350°C in a porcelain dish. The lower oxides of vanadium produced, together with vanadium(V) oxide, were oxidized by heating them with a small amount of nitric acid. The vanadium(V) oxide thus obtained was melted in a platinum crucible and crystallized by pouring out the melt on a copper plate.

Glasses of Sodium Vanadate-Phosphates.—Glasses of sodium vanadate-phosphates with various P/V ratios were prepared by melting mixtures of sodium metaphosphate (Graham salt), vanadium(V) oxide and sodium carbonate.

$$2x\mathrm{NaPO_3}+y\mathrm{V_2O_5}+y\mathrm{Na_2CO_3}$$

$$=2x\mathrm{NaPO_3}\cdot 2y\mathrm{NaVO_3}+y\mathrm{CO_2} \quad (1)$$

or

$$=(x+y)\mathrm{Na_2O}\cdot x\mathrm{P_2O_5}\cdot y\mathrm{V_2O_5}+y\mathrm{CO_2} \quad (2)$$

However, a part of the vanadium(V) oxide was reduced to vanadium(IV) oxide formally.

$$y\mathrm{V_2O_5}=(y-z)\mathrm{V_2O_5}+z\mathrm{V_2O_4}+z/2\mathrm{O_2} \quad (3)$$

In a platinum crucible a certain amount (15∼30 g.) of monosodium dihydrogen orthophosphate dihydrate was dehydrated and melted by heating and converted into a glass of sodium metaphosphate by cooling the melt in the platinum crucible. After the weight of the glass was measured, calculated amounts of vanadium(V) oxide and sodium carbonate were taken on the glass in the crucible. Then the mixture of these three materials was melted at 900°C for 1 hr. The melt was quenched by pouring it on a copper plate and by pressing it with another copper plate. By this procedure glasses of sodium vanadate-phosphates with P/V ratios (x/y in Eq. 1) of 1, 2, 3, 4, 7, 10, 50, 100 and 200 were prepared. The glasses had colors ranging from dark brown toward yellow with the increasing P/V ratio.

Crystals of Sodium Vanadate-Phosphates.—A melt obtained from a mixture of sodium metaphosphate, vanadium(V) oxide and sodium carbonate was crystallized by keeping it at 450∼500°C for 24 hr. By this treatment crystals of sodium vanadate-phosphates with P/V ratios of 7, 10 and 50 were prepared. All of the crystals are yellowish-green. By a similar treatment, the melts with P/V ratios of 3 and 4 were only partially crystallized.

Determination of Percentages of Vanadium(IV) in Relation to Total Vanadium.—An appropriate amount of sodium vanadate-phosphate was dissolved in 2 N sulfuric acid and titrated with 0.03 N potassium permanganate while being warmed on a water bath. After the titration with permanganate, the sample solution was titrated with 0.03 N ammonium iron(II) sulfate by the use of a few

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[1] E. Thilo and L. Koditz, *Z. anorg. u. allgem. Chem.*, **278**, 122 (1955); E. Thilo and K. Dostal, ibid., **298**, 100 (1958); I. Grunze, K. Dostal and E. Thilo, ibid., **302**, 221 (1959).

[2] L. F. Audrieth, J. R. Mills and L. E. Netherton, *J. Phys. Chem.*, **58**, 482 (1954).

[3] R. Jary, *Ann. chim.* (Paris) [13], **2**, 58 (1957).

[4] M. Munakata, S. Kawamura, J. Asahara and M. Iwamoto, *J. Ceram. Assoc. Japan* (*Yogyo Kyokai-shi*), **67**, 344 (1959).

drops of a diphenylamine solution as an indicator, which solution was made by dissolving about 0.5 g. of diphenylamine in 50 ml. of 85% phosphoric acid. Before the second titration, 3 ml. of 85% phosphoric acid should be added to each 100 ml. of the sample solution in order to mask the iron(III). The first titration corresponds to the amount of vanadium-(IV), and the second, to the total amount of vanadium. From these titrations the percentages of vanadium(IV) in relation to the total vanadium ($z/y \cdot 100$ in Eq. 3) were calculated.

Paper Chromatography.—The paper chromatographic method of Karl-Kroupa[5] was used for samples containing short-chain phosphates and trimetaphosphate, while that of Smith[6] was used for samples containing relatively long-chain phosphates. The acid solvent was made by mixing 735 ml. of isopropyl alcohol, a solution of 50 g. of trichloroacetic acid in 265 ml. of water, and 2.5 ml. of concentrated aqueous ammonia. The basic solvent was made by mixing 387 ml. of isopropyl alcohol, 200 ml. of isobutyl alcohol, 408 ml. of water, and 5 ml. of concentrated aqueous ammonia. Toyo No. 51A filter papers were used. The colorimetric determination of orthophosphate was done by Nakamura's method[7].

A paper area for each phosphate species was cut into pieces and transferred to a small glass-filter connected to a suction bottle. Then 3~4 ml. of 1 N aqueous ammonia was added to the glass filter; after a few minutes it was filtered into a volumetric flask of 25 ml. by the use of a suction pump. This procedure was repeated four times, and a total of 15 ml. of 1 N aqueous ammonia was used. To the solution in the flask, 3.88 ml. of 8 N sulfuric acid was added, and the flask was placed in a boiling water bath for 20 min. in order to hydrolyze all the condensed phosphates to orthophosphate. After the flask was cooled, 3.3 ml. of amidol reagent[7] and 1.7 ml. of molybdate reagent[7] were added. Then the volume was brought up to the 25 ml. mark with distilled water. After the flask had been kept at 20°C for 10 min., the absorbance of blue color was measured against a reagent blank at 750 mμ.

Results and Discussion

When a mixture of sodium metaphosphate, vanadium(V) oxide and sodium carbonate is melted, carbon dioxide and then another kind of gas are evolved. It was qualitatively confirmed that the gas is oxygen. On the other hand, solutions of the glasses or the crystals of vanadate-phosphates are green and discolor a dilute solution of potassium permanganate acidified with sulfuric acid. These facts indicate that a part of the vanadium(V) in the melt is reduced to vanadium(IV) by the evolution of oxygen.

When a melt of vanadate-phosphates with a P/V ratio of 3 is heated at 900°C for 1, 2, 3 or 4 hr., the resulting glasses contain about 19% of vanadium(IV) in relation to the total vanadium in all cases, as is shown in Table I. This fact means that a heating of 1 hr. is sufficient to achieve an equilibrium between vanadium(V) and vanadium(IV) at 900°C.

TABLE I. PERCENTAGES OF VANADIUM(IV) IN RELATION TO THE TOTAL VANADIUM IN THE GLASSES WITH P/V RATIO OF 3, PREPARED BY HEATING FOR 1~4 hr. AT 900°C

Heating time, hr.	V(IV), %
1	18.9
2	18.7
3	18.8
4	18.9

The percentages of vanadium(IV) in relation to the total vanadium in the glasses of vanadate-phosphates with various P/V ratios are shown in Table II. With an increasing P/V ratio, i. e., with a decrease in the absolute amount of vanadium, the percentages of vanadium(IV) increase and reach an almost nearly constant value, 37~38%, when the P/V ratio is larger than 50.

TABLE II. PERCENTAGES OF VANADIUM(IV) IN RELATION TO THE TOTAL VANADIUM IN THE GLASSES HAVING VARIOUS P/V RATIOS

P/V ratio	V(IV), %
1	4.5
2	11.4
3	18.9
4	22.8
7	30.1
10	33.8
50	37.4
100	38.0
200	37.8

The percentages of vanadium(IV) in relation to the total vanadium in the crystals of vanadate-phosphates with P/V ratios of 7, 10 and 50, which are shown in Table III, are always a little smaller than those of vanadium-(IV) in the glasses with the same P/V ratios.

TABLE III. PERCENTAGES OF VANADIUM(IV) IN RELATION TO THE TOTAL VANADIUM IN THE CRYSTALS HAVING VARIOUS P/V RATIOS

P/V ratio	V(IV), %
7	27.1
10	32.0
50	34.1

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[5] E. Karl-Kroupa, *Anal. Chem.*, **28**, 1091 (1956) and her private publication.

[6] M. J. Smith, *Ontario Research Foundation*, *Report* 5703 (1957).

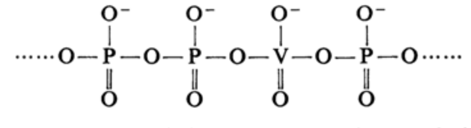
[7] M. Nakamura, *J. Agr. Chem. Soc. Japan* (*Nippon Nogeikagaku Kaishi*), **24**, 1 (1950).

TABLE IV. PHOSPHATE SPECIES FOUND IN THE AQUEOUS SOLUTIONS OF VARIOUS SODIUM VANADATE-PHOSPHATES

P/V	P, %								
	Ortho	Pyro	Tripoly	Tetra-poly	Penta-poly	Hexa-poly	Hepta-poly	Heigher poly	Tri-meta
Glasses									
1	89	11	0	0	0	0	0	0	0
2	19	65	15	0	0	0	0	0	0
3	12	63	22	4	0	0	0	0	0
4	8	33	9	15	11	9	0	14	0
7	2	15	9	8	1	8	8	48	0
10	3	11	5	3	2	7	10	59	0
Crystals									
7	6	23	8	4		5	5	0	50
10	3	17	7	2		3	2	7	60
50	2	4	0	0		0	0	0	94

The results of the paper chromatography for the determination of phosphate species in the aqueous solutions of the glasses and the crystals of vanadate-phosphates are summarized in Table IV. Almost all of these data were obtained by the paper chromatography with an acid solvent. Although by the use of the acid solvent trimetaphosphate can not be completely separated from tetrapoly- or pentapolyphosphate, two-dimensional paper chromatograms for the aqueous solutions of the glasses with P/V ratios of 1∼10 did not indicate the presence of ring phosphates such as trimeta- or tetrametaphosphate. Since the aqueous solutions of the crystals, on the contrary, contained trimetaphosphate, the total amount of tetrapoly-, pentapoly- and trimetaphosphate was determined by the use of the acid solvent, and the amount of trimetaphosphate was separately determined by the use of the basic solvent. The sum of tetrapoly- and pentapolyphosphate was calculated as the difference between these two figures.

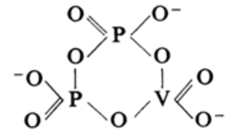
The data for the glasses in Table IV indicate that the contents of the longer chain phosphates increase with an increasing P/V ratio. If it is assumed that P–O–V linkages in the solid substances are hydrolyzed as soon as dissolved in water, it may be presumed that the glasses are composed of chain structures such as



$$\cdots\cdots\mathrm{O}-\underset{\underset{\mathrm{O}}{\|}}{\overset{\overset{\mathrm{O^-}}{|}}{\mathrm{P}}}-\mathrm{O}-\underset{\underset{\mathrm{O}}{\|}}{\overset{\overset{\mathrm{O^-}}{|}}{\mathrm{P}}}-\mathrm{O}-\underset{\underset{\mathrm{O}}{\|}}{\overset{\overset{\mathrm{O^-}}{|}}{\mathrm{V}}}-\mathrm{O}-\underset{\underset{\mathrm{O}}{\|}}{\overset{\overset{\mathrm{O^-}}{|}}{\mathrm{P}}}-\mathrm{O}\cdots\cdots$$

where vanadium(V) atoms are inserted into the phosphate chain.

Since a melt having a composition of sodium metaphosphate is crystallized as sodium trimetaphosphate under the same conditions as those used for the preparation of the crystals of sodium vanadate-phosphates, it is easy to surmise that crystals with P/V ratios of 7, 10 and 50 are mainly composed of trimetaphosphate, as is shown in Table IV. With an decreasing P/V ratio, i. e., with an increase in the absolute amount of vanadium, the amounts of trimetaphosphate decrease and those of pyrophosphate increase. Moreover, the pyrophosphate found in the solutions of the crystals are predominant in comparison with the other chain phosphates. These facts indicate that the pyrophosphate is probably derived from the hydrolysis of the following vanadate-phosphate ring:



At the present stage of investigation, it is not possible to determine, however, whether the chain phosphates other than the pyrophosphate are derived from amorphous substances mixed in the crystals.

The data in Table IV show that the main component in the case of the glass with a P/V ratio of 1 is orthophosphate. This fact may indicate that the glass is composed of a chain structure of alternate P–O and V–O linkages. The aqueous solutions of the glasses with P/V ratios of 2∼10 contain predominant amounts of pyrophosphate in comparison with the other short-chain phosphates. From the fact it seems probable that the trimeta-vanadate-phosphate ring described in the case of the crystals is present also in the glasses.

In the aqueous solutions of the glasses, the number of chain phosphates longer than octapolyphosphate increases with an increasing P/V ratio. Although the aqueous solutions of the glasses with P/V ratios of 50, 100 and 200 could not be analyzed quantitatively by paper chromatography, almost all of the phosphorus were found as non-moving spots in their paper chromatograms developed with the acid solvent.

The role of vanadium(IV) in the glasses and the crystals has not been clear. However, from the fact that vanadyl ions VO^{2+} are most stable in crystals and solutions of vanadium(IV) salts, the vanadium(IV) in the vanadate-phosphates may also be present as vanadyl ions and may play a role as a cation like sodium ions.

An X-ray diffraction pattern of the crystal with a P/V ratio of 50 is identical with that of sodium trimetaphosphate. This means that the presence of the vanadate, which is a minor constituent in this case, has not a great effect on the pattern of sodium trimetaphosphate. On the contary, X-ray patterns of crystals with P/V ratios of 7 and 10 are quite different from those of both sodium trimetaphosphate and sodium metavanadate.

Summary

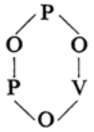
Glasses of sodium vanadate-phosphates with P/V ratios of 1～200 were prepared from mixtures of sodium metaphosphate, vanadium(V) oxide and sodium carbonate. Crystals of sodium vanadate-phosphates with P/V ratios of 7, 10 and 50 were also prepared.

During the preparation of the glasses and the crystals, a part of the vanadium(V) is reduced to vanadium(IV). The percentages of vanadium(IV) in relation to the total vanadium increase with an increasing P/V ratio.

From the paper chromatographic analyses of the aqueous solutions of the glasses and the crystals, it may be presumed that the glasses are mainly composed of chain structures such as

……O—P—O—P—O—V—O—P—O—……

and that the crystals contain considerable amounts of a vanadate-phosphate ring as follows:



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