The Composition of Strong Phosphoric Acids

By Shigeru OHASHI and Hiroko SUGATANI

(Received June 6, 1957)

Since several years ago new analytical methods[1] for the determination of carbon, nitrogen, sulfur and so on by the use of strong phosphoric acids as reaction media have been investigated in the authors' laboratory and a preliminary study on the composition of strong phosphoric acids was already reported[2].

The composition of strong phosphoric acids having 72 to 89 wt. % phosphorus(V) oxide was studied by Bell[3] who employed the so-called zinc titration method for the analysis of pyro- and tripolyphosphate. Thereafter many analytical methods were developed for the determination of various types of condensed phosphate; filterpaper chromatography[4], anion-exchange chromatography[5], pH-titration method[6], X-ray diffractometry[7], isotope dilution method[8], cobaltcomplex method[9], and infrared absorption spectrometry[10].

Higgins and Baldwin[11] used the anion-exchange chromatography, which was presented by Beukenkamp, Rieman III, and Lindenbaum[5], for their study on the composition of strong phosphoric acids which were prepared by dehydration of 85 wt. % orthophosphoric acid at the constant temperatures, 100° and 176°C. During the course of the present work Huhti and Gartaganis[12] published their report on the composition of strong phosphoric acids having 68.8 to 86.3 wt. % phosphorus (V) oxide, which were analyzed by the method of filterpaper chromatography.

In the present paper the composition of strong phosphoric acids containing about 67 to 80 wt. % phosphorus (V) oxide, which were prepared from 85 wt. % orthophosphoric acid under various conditions, was investigated in detail by the use of the anion-exchange chromatography[5] combined with the usual molybdenum-blue colorimetric analysis for orthophosphate.

Experimental

Preparation of Strong Phosphoric Acids.— About 30 g. of 85 wt. % orthophosphoric acid was heated on an electric heater as shown in Fig. 1 until a thermometer immersed in the acid indicated a definite temperature, 161°, 183°, 203°, 220°, 244°, 260°, 280°, 301°, 340°, or 380°C, respectively (sample Nos. 1 to 10 in Table I). The time required for the dehydration was eight, sixteen, twenty five, thirty one, and sixty minutes for the temperatures, 183°, 220°, 301°, 340°, and 380°C, respectively. In a similar way about 30g. and 300 g. of 85 wt. % orthophosphoric acid were

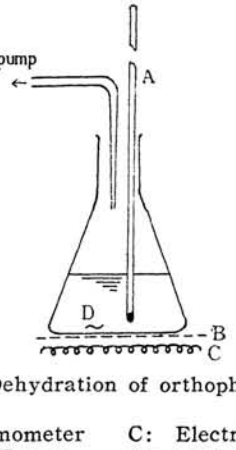

Fig. 1. Dehydration of orthophosphoric acid.
A: Thermometer
B: Wire Gauze
C: Electric Heater
D: Platinum Wire

---

1) T. Kiba, S. Ohashi, T. Takagi and Y. Hirose, *Japan Analyst*, **2**, 446 (1953); S. Ohashi, This Bulletin, **28**, 171, 177, 537, 585 and 645 (1955); T. Kiba, T. Takagi, Y. Yoshimura and I. Kishi, ibid., **28**, 641 (1955); T. Takagi, *Japan Analyst*, **4**, 624 (1955); S. Ohashi and H. Makishima, This Bulletin, **29**, 700 (1956); T. Kiba and I. Kishi, ibid., **30**, 44 (1957); S. Takagi and N. Hayashi, *J. Chem. Soc. Japan, Pure Chem. Sec.*, **78**, 445 (1957).

2) S. Ohashi, This Bulletin, **28**, 537 (1955).

3) R. N. Bell, *Ind. Eng. Chem.*, **40**, 1464 (1948); cf. R. N. Bell, A. R. Wreath and W. T. Curless, *Anal. Chem.*, **24**, 1997 (1952).

4) J. P. Ebel et al., *Compt. rend.*, **233**, 415 (1951), **242**, 647 (1956) and *Bull. Soc. Chim. France*, **1953**, 991, 998, 1089 and 1096; J. P. Crowther, *Anal. Chem.*, **26**, 1383 (1954); E. Karl-Kroupa, ibid., **28**, 1091 (1956).

5) J. Beukenkamp, W. Rieman III and S. Lindenbaum, ibid., **26**, 505 (1954); S. Lindenbaum, T. V. Peters, Jr., and W. Rieman III, *Anal. Chim. Acta*, **11**, 530 (1954).

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

7) A. J. Mabis and O. T. Quimby, ibid., **25**, 1814 (1953).

8) O. T. Quimby, A. J. Mabis and H. W. Lampe, ibid., **26**, 661 (1954).

9) H. W. McCune and G. J. Arquette, ibid., **27**, 401 (1955).

10) D. E. C. Corbridge and E. J. Lowe, ibid., **27**, 1383 (1955).

11) C. E. Higgins and W. H. Baldwin, ibid., **27**, 1780 (1955).

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

TABLE I

COMPOSITION OF STRONG PHOSPHORIC ACIDS

Sample No.	Initial Weight g.	Temp. °C	Specific Gravity at 15°C	Total P_2O_5 wt. %	Ortho H_3PO_4 wt. %	Pyro $H_4P_2O_7$ wt. %	Tripoly $H_5P_3O_{10}$ wt. %	Tetrapoly $H_6P_4O_{13}$ wt. %	Water H_2O wt. %
1	25.68	161	1.77	62.5	86.3	—	—	—	13.7
2	26.37	183	1.81	66.7	90.9	1.1	—	—	8.0
3	28.63	203	1.84	68.5	89.9	4.4	—	—	5.8
4	29.28	220	1.87	68.9	90.5	4.2	—	—	5.3
5	28.14	244	1.89	69.2	90.0	5.0	—	—	5.0
6	28.92	260	1.90	71.8	89.8	8.1	0.3	—	1.8
7	28.79	280	1.92	75.1	66.1	29.3	4.6	—	—
8	29.24	301	1.95	76.2	53.8	39.5	6.8	—	—
9	33.52	340	2.03	78.3	29.4	47.4	22.7	0.5	—
10	32.06	380	2.08	80.1	16.7	38.6	24.8	19.9	—
11	30	300	1.99	78.4	29.8	45.4	20.4	4.4	—
12	300	301	2.07	77.2	44.4	39.8	12.3	3.6	—
13	10.70	140[a]	1.92	74.5	74.1	23.5	2.5	—	—
14	10	140[a]	1.93	74.7	69.4	28.2	2.1	0.3	—

[a] at the constant temperature, 140°±2°C.

dehydrated by raising the temperature of the liquid up to 300°C for sixty minutes (samples Nos. 11 and 12 in Table I). The latter is the so-called "300°C-strong phosphoric acid", which has been used for many analytical purposes in the authors' laboratory. There was no apparent attack on the glass in the preparation described above.

On the other hand about 10 g. of 85 wt. % orthophosphoric acid was taken in a platinum crucible and dehydrated by heating in a constant temperature oven at 140°±2°C for twenty one and thirty one hours, respectively (sample Nos. 13 and 14 in Table 1).

Specific Gravities of the Strong Phosphoric Acids were measured using a 1-ml. or 2.5-ml. specific gravity bottle at 15°C.

Analysis of the Strong Phosphoric Acids.—A 0.2 to 0.8 g. portion of the strong phosphoric acid was weighed in a weighing tube, dissolved in 30 ml. of distilled water in 100-ml. volumetric flask, immediately neutralized to phenolphthalein with 1 N sodium hydroxide and the volume adjusted to the mark with distilled water. An aliquot of this solution, 2 ml. was poured into a column filled with resin. Anion exchanger, Dowex 1 was used under the following conditions: 120 to 200 mesh, 8% cross-linked, a column of 0.79 sq. cm. ×20 cm., exchange capacity of 2.28 meq./g., 2.62 g. in the dry state, chloride form. Elutions of individual phosphates were made by the method of Higgins and Baldwin[11]. Using a flow rate of 0.5 to 0.7 ml./min., orthophosphate was removed with 0.05 M hydrochloric acid, pyrophosphate with 0.20 M potassium chloride, tripolyphosphate with 0.27 to 0.35 M potassium chloride, and tetrapolyphosphate with 0.35 to 0.50 M potassium chloride.

By the first run the phosphate contained in each fraction of 5 ml. of eluate solution was determined colorimetrically by means of Nakamura's molybdenum-blue method[13]. Although orthophosphate was directly determined by the colorimetry, polyphosphates were hydrolyzed by heating with diluted sulfuric acid to orthophosphate before the colorimetric determination. A typical elution curve is shown in Fig. 2. In the second run, after the resin was again loaded with the same sample solution, the quantity of each eluant solution, required to separate the phosphate mixture, was let flow through the column, collected in a volumetric flask, and diluted to the mark with distilled water. An appropriate aliquot of the solution, after being hydrolyzed and concentrated, if necessary, was subjected to determination of phosphorus as previously described.

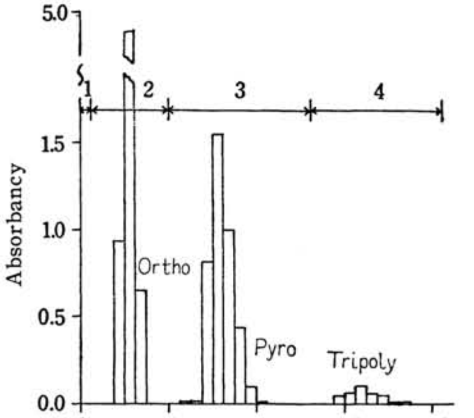

Fig. 2. Elution curve of sample No. 8.
1: Sample soln. and water
2: 0.05 M HCl
3: 0.20 M KCl
4: 0.35 M KCl

---

[13] M. Nakamura, *J. Agr. Chem. Soc. Japan*, **24**, 1 (1950).

Results and Discussion

The results of the analyses of the strong phosphoric acids are shown in Table I. This indicates that the formation of pyro-, tripoly- and tetrapolyphosphoric acid starts at the concentration of phosphorus (V) oxide, around 67, 72 and 75 wt. %, respectively. The so-called "300°C-strong phosphoric acid" in the authors' laboratory, the sample No. 12, is composed of 44.4 wt. % orthophosphoric acid, 39.8 wt. % pyrophosphoric acid, 12.3 wt. % tripolyphosphoric acid, and 3.6 wt. % tetrapolyphosphoric acid. However, even the strong phosphoric acids which were prepared by heating orthophosphoric acid up to the same temperature, 300°C, have quite different compositions depending upon the weight of orthophosphoric acid taken and the elevation rate of the temperature. These facts may be clarified by comparing the results of the sample Nos. 8, 11 and 12.

Higgins and Baldwin[11] heated orthophosphoric acid at the constant temperature, 176°C for sixteen hours and obtained a mixture of 51 wt. % orthophosphoric acid, 38 wt. % pyrophosphoric acid, 9 wt. % tripolyphosphoric acid, 2 wt. % tetrapolyphosphoric acid, and 0.2 wt. % pentapolyphosphoric acid. No change in the composition was noted on prolonged heating up to 32.5 hours at 176°C. Therefore, the difference between the composition of the sample Nos. 13 and 14 in Table I, which were prepared by heating at 140°±2°C, may be due to the fluctuation of the temperature.

In Fig. 3 the relation between the composition of the strong phosphoric acids and their contents of phosphorus (V) oxide are illustrated. Generally they coincide with the data obtained by Bell[3], Higgins and Baldwin[11], and Huhti and Gartaganis[12], even if the strong phosphoric acids were prepared under different conditions. As indicated by Bell[3] and Huhti and Gartaganis[12], this means that a dynamic equilibrium between the component acids is set up, when the strong phosphoric acids are prepared by heating. However, Bell's data in higher phosphorus (V) oxide content may not be correct, because he did not determine separately the polyacid components higher than tripolyphosphoric acid. In the study by Huhti and Gartaganis small quantities of penta-, hexa- and heptapolyphosphoric acid were determined in the range from 78 to 80 wt. % phosphorus (V) oxide, but the present authors were not able to find them. In this respect the method of anion-exchange chromatography should be furthermore examined for the determination of higher polyphosphates.

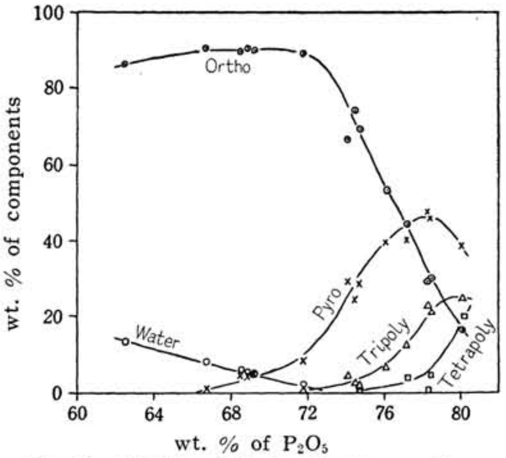

Fig. 3. Relation between the composition of the strong phosphoric acids and the contents of phosphorus(V) oxide.

During the course of the present investigation Parks and Van Wazer[14] published their treatise, in which a reorganization theory for the condensed phosphates as well as the strong phosphoric acids was developed. According to their theory for the strong phosphoric acids, in the general case, all five of the structural units, i. e. branching PO_4 units, middle PO_4 units, end PO_4 units, orthophosphoric acid units, and unreacted water molecule units may be present, with mole fractions b, m, e, o and u. All of the combinations whereby these units can interchange roles with each other are given by the following equations with the equilibrium constants.

$$2m=b+e \qquad K_1=b\cdot e/m^2 \qquad (1)$$

$$2e=m+o \qquad K_2=m\cdot o/e^2 \qquad (2)$$

$$2o=2e+u \qquad K_3'=(2e)\cdot u/o^2 \qquad (3)^{15)}$$

In addition to the equations (1), (2) and (3), there are two other equations (4) and (5).

$$R=H_2O/P_2O_5=H/P$$

$$=(3o+2e+m+2u)/(b+m+e+o) \qquad (4)$$

$$b+m+e+o+u=1 \qquad (5)$$

---

14) J. R. Parks and J. R. Van Wazer, *J. Am. Chem. Soc.*, in press.

15) For this equilibrium another equilibrium constant $K_3=e^2\cdot u/o^2$ may be supposed, but the values of K_3 calculated from the experimental data were not constant in Parks and Van Wazer's study.

From the experimental data obtained by Huhti and Gartaganis[12] it was assumed that $K_1=1.0\times10^{-3}$, $K_2=8\times10^{-2}$, and $K_3'=2.0\times10^{-2}$ on a mole fraction basis. The theoretical curves of mole fractions of *b*, *m*, *e*, *o* and *u* were plotted as a function of *R* on the assumption mentioned above. These curves are shown in Fig. 4. The experimental data obtained by Huhti and Gartaganis agreed with the theoretically derived curves, although the data covered only the range from $R=1.2$ to $R=3.6$. The experimental data of the present study are shown as individual points in Fig. 4 and they also agree very well with the theory at least in the range from $R=2.0$ to $R=4.0$. This may prove the correctness of Parks and Van Wazer's theory.

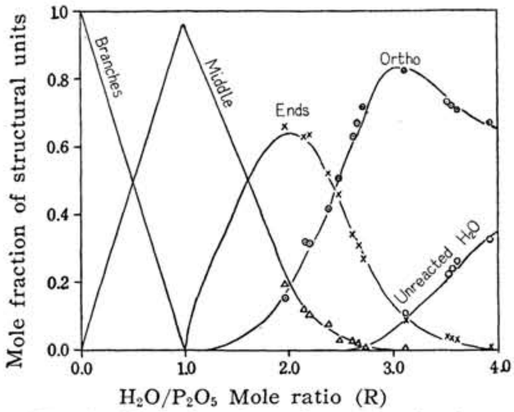

Fig. 4. Mole fractions of structural units as a function of H_2O/P_2O_5 mole ratio.

Summary

The strong phosphoric acids in the range from 67 to 80 wt. % phosphorus(V) oxide were analyzed by the anion-exchange chromatography combined with the usual molybdenum-blue colorimetry. The so-called "300°C-strong phosphoric acid" which has been used for many analytical purposes in the authors' laboratory is composed of 44.4 wt. % orthophosphoric acid, 39.8 wt. % pyrophosphoric acid, 12.3 wt. % tripolyphosphoric acid, and 3.6 wt. % tetrapolyphosphoric acid. It was found that the relation of mole fractions of middle PO_4 units, end PO_4 units, orthophosphoric acid units, and unreacted water molecule units versus the mole ratio H_2O/P_2O_5 agrees with the reorganization theory for the strong phosphoric acids, presented by Parks and Van Wazer.

The authors wish to thank Professor T. Kiba for many helpful suggestions and criticism. They also thank the Ministry of Education for the financial support of this research.

Department of Chemistry
Faculty of Science
Kanazawa University
Kanazawa