# *On Solvolysis of α-Phosphorus(V) Oxide*

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It has been well-known[1-3] since 1940 that phosphorus(V) oxide exists in three crystalline modifications ($\alpha$, $\beta$, $\gamma$)[4] and that the crystal of the $\alpha$-modification is composed of $P_4O_{10}$ molecules in which four phosphorus atoms are at the apices of a tetrahedron and are bonded to one another with six P–O–P linkages[1,2,5], as is shown in Fig. 1. Water reacts violently

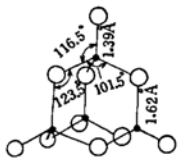


Fig. 1. The structure of the molecule $P_4O_{10}$.
○ Oxygen atoms • Phosphorus atoms

with it, and organic solvents such as alcohols and acetone[6] also indicate some chemical action. As regards the reaction process of $\alpha$-phosphorus(V) oxide with water and the resulting products thereof, much information is available[7-11], but little is known about the reactions with organic solvents.

The present authors attempted to clarify the general reaction mechaniem of $\alpha$-phosphorus (V) oxide to which special attention was given to the solvolytic opening of the P–O–P linkages in this molecule and the accompanying condensation processes of phosphate radicals. Experiments were conducted along three lines: (a) direct hydrolysis with a large quantity of pure water, (b) solvolysis with organic solvents (e. g. ethanol and acetone) which are miscible with water and have some reaction with the oxide and (c) hydrolysis of the oxide dispersed in organic solvents which are non-reactive and able to hold a limited amount of water.

## Experimental

**Materials.**—Purification by subliming guaranteed reagent of $\alpha$-phosphorus(V) oxide with simple

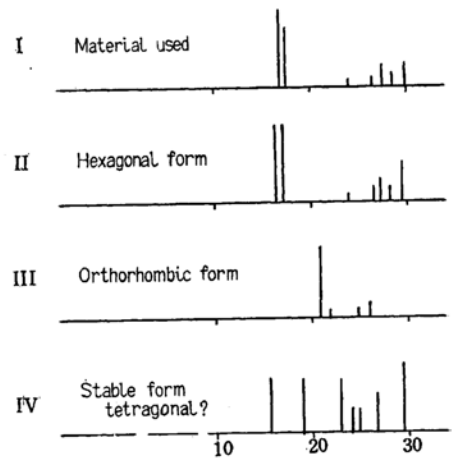


Fig. 2. The experimental X-ray diagram (I) of reagent $\alpha$-phosphorus(V) oxide compared with those data (II~IV) of polymorphic forms of phosphorus oxide by Hill et al.[2].
Experimental conditions:
Cu $K_\alpha$ (Ni filter)
35 KVP—15 mA
Slit 0.2-$2^1/_2$-$2^1/_2$, 16-1-2
Scan. sp. 4°/min.
Ch. sp. 1 cm./min.

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1) H. C. J. deDeker and C. H. MacGillavry, *Rec. trav. chim.*, **60**, 153 (1941); H. C. J. deDeker, ibid., 413.
2) W. L. Hill, G. T. Faust and S. B. Hendricks, *J. Am. Chem. Soc.*, **65**, 794 (1943).
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4) The three crystalline modifications of phosphorus-(V) oxide were designated by deDeker et al. as $S_1$, $S_2$ and $S_3$, and by Thilo et al., as M., R. and S.
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6) T. Kuwata, "Yozai", Maruzen Co. (1951), p. 256.
7) R. N. Bell, L. F. Audrieth and O. F. Hill, *Ind. Eng. Chem., Anal. Ed.*, **44**, 568 (1952).
8) E. Thilo and W. Widker, *Z. anorg. allgem. Chem.*, **277**, 27 (1954).
9) A. E. R. Westman, A. E. Scott and J. T. Pedley, *Chemistry in Canada*, Oct. 1 (1952).
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equipment proved to be unsuitable because of the extraordinarily strong absorptive power of the sublimate against traces of moisture remaining in dried vessels. However, as this material was confirmed to be very pure by X-ray examination (as shown in Fig. 2) it was used without further purification.

**Organic Solvents.** — Diethyl ether and benzene were dried with sodium metal, acetone with anhydrous sodium sulfate and ethanol with calcium oxide. The diethyl ether, benzene and acetone were of reagent grade and ethanol was of guaranteed grade. They were distilled at least twice and used dry or after a definite weight or volume of water had been added.

**Reaction Procedure.**—Each solvent was weighed in a beaker or in a large weighing bottle[12], kept at 0°C and agitated vigorously with a magnetic stirrer. Then 0.5 g. of α-phosphorus(V) oxide was added to the solvent in small portions using a special vessel equipped with a closely fitting lid worked by a spring so as to cause complete dispersion[13].

When water or any solvent miscible with water, for example, acetone or ethanol with or without added water, was used, stirring was continued until the added oxide thoroughly dissolved, the resulting solution was still kept at 0°C and neutralized with 1 N sodium hydroxide[14] (indicator; litmus test paper). In the case of pure water 10 ml. was used each time. Since α-phosphorus(V) oxide went almost completely into solution[15], no treatment was necessary before spotting 0.01 ml. or 0.02 ml. of the sample with a micropipette on a chromatographic paper along a starting line. Different species of the condensed phosphates in this solution were successfully separated. At the same time, a 2 ml. aliquot of the sample solution was taken in order to determine the total phosphorus-(V) concentration by colorimetric analysis. In the case of acetone or ethanol with or without added water (20 ml. in total volume), α-phosphorus(V) oxide dissolved only to a limited extent, and the remaining precipitate had to be separated from the solution with decantation and dissolved in 20 ml. of pure water. After the volume had been adjusted, the contents of the various condensed phosphates, and the total phosphate concentration were determined for these two solutions. On the other hand, in the case of diethyl ether (13 ml.) or benzene (10 ml.), α-phosphorus(V) oxide was dispersed in it as perfectly as possible, and, the mixture being kept in vigorous agitation with a magnetic stirrer, 10 ml. of water was added, and the resulting solution was neutralized with 1 N sodium hydroxide, and then transferred to a separating funnel. The organic phase was removed from the aqueous phase and washed with 2 ml. of water; it was discarded, for no trace of phosphorus(V) was found in it. The aqueous phase was added to the above wash water, and was subjected to analysis for the various condensed phosphates and the total phosphate concentration.

**The Separation of Various Species of Condensed Phosphates by Filter Paper Chromatography.**— Various condensed phosphates differing in degree and mode of polymerization were separated by ascending chromatography on filter paper. The method has been studied by many workers[9,16-21]. In the present work, eleven kinds of acidic solvent and six kinds of basic solvent already reported were tested with Toyo Roshi No. 5B for quantitative analysis[22], and the two following solvents were chosen for their most effective separating ability. Acidic solvent: a mixture of propan-2-ol (70 ml.), water (30 ml.), trichloroacetic acid (5 g.) and concentrated aqueous ammonia (0.3 ml.). Basic solvent: a mixture of isobutanol (30 ml.), ethanol (30 ml.), water (39 ml.) and concentrated aqueous ammonia (1 ml.). $R_f$ values are given in Table I. For further work, experimental conditions were made as follows; length of the filter paper, 40 cm.; width, 2.5 cm.; time of chromatographic development, about 20 hr.; temperature, 10~20°C (room temperature). Lower ends of filter papers were narrowed after the method of Thilo et al.[19a]. The chromatographic separation seemed to improved by this cutting. Each condensed phosphate distributed in bands on a chromatogram was identified by Crowther's method[17c].

**Colorimetric Estimation of Each Condensed Phosphate.** — The condensed phosphates separated in bands on each chromatogram were determined by Crowther's method[17c] by the following procedure. Bands were cut out, soaked with 10 ml. of 1 N aqueous ammonia and eluted by warming on a

12) When dry or volatile solvent was used, reaction was performed in a large weighing bottle with a fitted stopper to prevent moist air from entering or the solvent from evaporating.

13) α-Phosphorus(V) oxide must be kept moisture-tight during the operation. The above-mentioned vessel, originally designed as a receptacle of "Ajinomoto powder", was obtained from the Ajinomoto Co., and was found to be very suitable for this purpose.

14) In the case of solvolysis with a large amount of water, the resulting solution was almost clear. This solution was subjected to moderate neutralization with Amberlite IRC-50, Na-form resin, or with sodium carbonate, so that the hydrolysis that might otherwise proceed during this procedure could be prevented. But these three neutralizing procedures with respective agents did not show any difference in results, as is shown in Table II.

15) A slight turbidity may appear in the solution, but it can be dispersed uniformly in a colloidal form and made to disappear when the solution is stirred sufficiently.

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17) a) A. E. R. Westman and A. E. Scott, *Nature*, **168**, 740 (1951); b) A. E. R. Westman and J. Crowther, *J. Am. Cer. Soc.*, **37**, 420 (1954); c) J. Crowther, *Anal. Chem.*, **26**, 1383 (1954).

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19) E. Karl-Kroupa, *Anal. Chem.*, **28**, 1091 (1956).

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

21) G. G. Berg, *Anal. Chem.*, **30**, 213 (1958).

22) Filter papers often contain phosphorus(V) which can be detected by a qualitative method or with colorimetric analysis of eluted solution. Toyo Roshi No. 52 for chromatography contains substances which reduce ammonium molybdate during the procedure of phosphorus(V) detection. In Toyo Roshi No. 53 or No. 54 for chromatography, this was not noticed, but by the use of No. 54 paper, separation of various species of condensed phosphates was notably poor. In this work, No. 53 paper was also used.

TABLE I. SEPARATION OF VARIOUS CONDENSED PHOSPHATES BY ASCENDING CHROMATOGRAPHY WITH THE USE OF TWO KINDS OF SOLVENT

Filter paper; TOYO ROSHI No. 5B for quantitative analysis.

| Solvents | pH | Distances from base to front cm. | Time of development hr. | $R_f$ | | | | | | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Ortho- | Pyro- | Tripoly- | Trimeta- | Tetra-meta- | Highpoly- | |
| Acidic | 1.65 | 20.6 | 9.67 | 0.75 | 0.52 | 0.38 | 0.26 | 0.12 | 0 | 18b, 20 |
| Basic | 11.35 | 19.2 | 8.5 | 0.37 | 0.28 | 0.25 | 0.59 | 0.47 | 0 | 18b |

* All phosphates were used in the form of sodium salts. Standard substances were sodium salts. Test samples were neutralized with sodium hydroxide, sodium carbonate or sodium-form resin. But as the hydrogen ion concentration of chromatographic solvents was adjusted with aqueous ammonia, sodium may have been replaced by ammonium during the development process. In our experiments, the appearance of a spot of another phosphate species was very often noticed, especially in a basic solvent. This additional spot was confirmed to correspond to amomnium salt, for when the sodium in the phosphate had been replaced by ammonium through ion exchange resin column of Amberlite IR-120 ammonium-form, this spot alone was observed.

** The composition of the solvents are described in the text.

TABLE II. DISTRIBUTION OF PHOSPHORUS AMONG THE SOLVOLYSIS PRODUCT OF PHOSPHORUS(V) OXIDE BY A LARGE AMOUNT OF ICE WATER

| No. | Neutralizing agent | $PO_4^{3-}$ | $P_2O_7^{4-}$ | $P_3O_{10}^{5-}$ | $(PO_3)_3^{3-}$ | $(PO_3)_4^{4-}$ | Highpoly | Chromatographic solvent |
|---|---|---|---|---|---|---|---|---|
| 1 | NaOH | 2.0 | 2.1 | 2.7 | 14.1 | 60.1 | 19.0 | Acidic |
| 2 | $Na_2CO_3$ | 1.5 | 1.8 | 2.2 | 12.9 | 48.0 | 33.7 | Acidic |
| 3 | Resin | | 7.1 | | 15.2 | 60.2 | 17.4 | Acidic |
| 4 | Resin | | 26.7*** | | | 64.5 | 8.9*** | Basic |
| 5 | Resin | 2.0 | 1.5 | 4.6 | 16.0 | 66.0 | 10.3 | Acidic |
| 6 | Resin | 2.2 | 3.5*** | 9.1*** | 14.0 | 66.0 | 6.0*** | Basic |
| (Average of the above 2 lines) | | 2.1 | 2.5 | 6.8 | 15.0 | 66.0 | 8.2 | |
| 7 | NaOH | 2.3 | 1.5 | 4.5 | 12.9 | 61.3 | 17.4 | Acidic |
| 8 | NaOH | 2.6 | 2.0 | 2.3 | 16.2 | 58.5 | 18.3 | Acidic |
| (Total average) | | 2.1 | 2.1 | 4.2 | 14.5 | 60.0 | 16.4 | |

* Data from No. 5 to No. 8: Average of two determinations.

** Figures in this Table are the values of percentage distribution of phosphorus among respective phosphates.

*** During separation by filter paper chromatography, hydrolysis of the condensed phosphates seemed to advance more by the use of basic solvent than by the use of the acidic solvent. Accordingly, use of the basic solvent was avoided except in the experiment with a large amount of water.

water bath for 1 hr. The eluted sample solutions were treated with the molybdenum reagent in the ordinary way. The absorbance due to molybdenum blue was measured by a Hitachi EPU-2A type spectrophotometer at 830 m$\mu$ in glass cells with a 1 cm. light path using distilled water as the reference.

## Results

**Solvolysis (or Direct Hydrolysis) by a Large Quantity of Water.**—The main product in this case was tetrametaphosphoric acid mounting up to ca. 60% of phosphorus in agreement with the results of Bell et al.[7], Thilo et al.[8] and Westman et al.[9]. The detailed numerical records of contents of each condensed phosphate produced by this direct action are given in Table II.

**Solvolysis by Acetone.**—The ratio of acetone to water was varied as follows: 10 : 0, 9.5 : 0.5, 9.0 : 1.0, 5.0 : 5.0, 0 : 10 by volume. The solvolysis by pure acetone gave 28.5% of tetrametaphosphoric acid and 42% of highpolyphosphoric acid as the major product. The percentage of tetrametaphosphoric acid increased with the water content of the solvent. The results are illustrated in Fig. 3.

**Solvolysis by Ethanol.**—The ratio of ethanol to water was varied in the same way as for acetone and water. $\alpha$-Phosphorus(V) oxide reacted with anhydrous ethanol and most of phosphorus(V) changed into pyrophosphoric acid, less than 5% of it becoming highpolyphosphoric acid and none turning into tetrametaphosphoric acid. Up to 50% of water

TABLE III. DISTRIBUTION OF PHOSPHORUS AMONG THE HYDROLYSIS PRODUCT OF PHOSPHORUS(V) OXIDE WITH ETHYL ETHER AND BENZENE AS DISPERSING AGENT

| $P_4O_{10}$ : $H_2O$ | Dispersing agent | $PO_4^{3-}$ | $P_2O_7^{4-}$ | $P_3O_{10}^{5-}$ | $(PO_3)_3^{3-}$ | $(PO_3)_4^{4-}$ | Highpoly | Number of highpoly spot |
|---|---|---|---|---|---|---|---|---|
| Dehydrated | Ether | 1.76 | 1.02 | 0 | 14.4 | 68.3 | 14.4 | 2 |
| 1 : 2 | Ether | 2.42 | 2.42 | 0 | 12.4 | 50.3 | 32.2 | 2 |
| 1 : 10 | Ether | 1.88 | 1.07 | 3.44 | 10.2 | 55.3 | 28.9 | 3 |
| Dehydrated | Benzene | 1.56 | 0.96 | 1.66 | 11.4 | 65.7 | 18.6 | 2 |
| 1 : 1 | Benzene | 2.06 | 1.13 | 1.68 | 10.6 | 57.5 | 27.1 | 1 |
| 1 : 2 | Benzene | 1.93 | 0.99 | 1.86 | 11.4 | 58.5 | 25.6 | 1 |

* Data with ether: Average of four determinations.
Data with benzene: Average of two determinations.

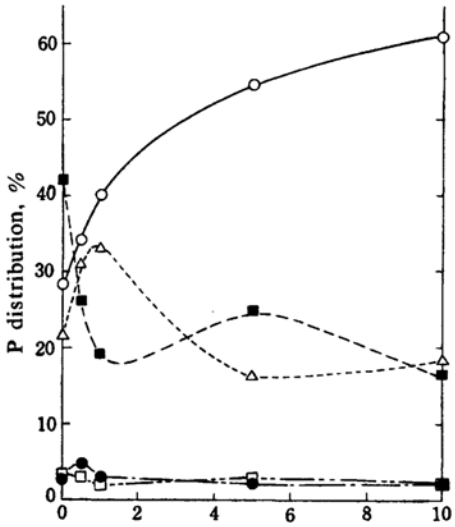


Fig. 3. Distribution of phosphorus among the solvolysis product of phosphorus(V) oxide by acetone and water-in-acetone system as solvent.
● Orthophosphate
□ Pyrophosphate
△ Tripoly- and trimetaphosphates
○ Tetrametaphosphate
■ Highpolyphosphate

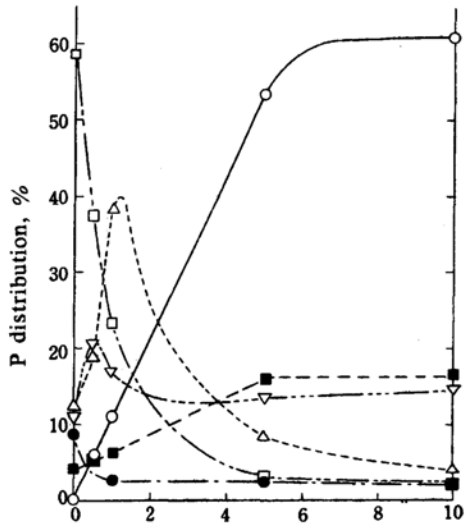


Fig. 4. Distribution of phosphorus among the solvolysis product of phosphorus(V) oxide by ethanol and water-in-ethanol system as solvent.
● Orthophosphate
□ Pyrophosphate
△ Tripolyphosphate
▽ Trimetaphosphate
○ Tetrametaphosphate
■ Highpolyphosphate

content, the yield of tetrameta- and highpolyphosphoric acid is linerly related to the water content, the yield of pyrophosphoric acid being rapidly decreased with increase in water content. The entire result is shown in Fig. 4.

**Hydrolysis with Diethyl Ether and Benzene as Dispersing Agents.**—It was considered that when these solvents were used in a completely anhydrous state, results might differ essentially from what would be the case when they contained initially a minute amount of water. However, results did not show the expected tendency distinctly, as may be seen in Table III.

## Discussion

The molecular structure of α-phosphorus(V) oxide can be conveniently represented by a square formula I in Fig. 5, in which four P=O bonds are at the four corners and six P–O–P linkages are shown by four sides and two diagonals.

The P=O bonds are very stable as indicated by the short distances shown in Fig. 1, and they remain unaffected throughout the reactions dealt with in this study. Only the P–O–P linkages are attacked by reactive solvent molecules. Reaction of α-phosphorus(V) oxide

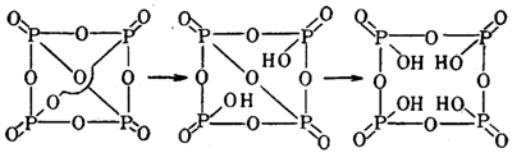


Fig. 5. Formulation of the process of tetrametaphosphoric acid formation.

with a large quantity of water, yielding tetrametaphosphoric acid as a principal product, can be formulated as shown in Fig. 5. The first water molecule approaching the oxide molecule opens any one of the six P–O–P linkages and produces an intermediate hydrolyzate (II), which is attacked by the second water molecule in succession. The fact that the main product is III can be explained by assuming that the weakest P–O–P linkage in II is the one situated diagonally opposite. This is quite easy to understand because only this P–O–P linkage is left to be strained owing to the bond angles of phosphorus atoms. Moreover, as the molecule of tetrametaphosphoric acid (III) has a fairly symmetrical structure, it is sufficiently stable and resists further attack of water molecules; it can be detected practically intact after the hydrolysis experiment. When the oxide reacts with alcohol, reaction proceeds I–IV–V–VI as shown in Fig. 6, yielding pyrophosphoric acid by the hydrolysis of the rather unstable ester formed. The reason why V receives further attack is attributable to its asymmetrical structure.

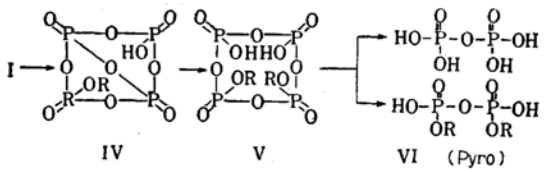


Fig. 6. Formulation of the process of pyrophosphoric acid formation.

A small quantity of trimeta- and tripolyphosphoric acids together with a still smaller quantity of orthophosphoric acid appearing in this case is explained as owing to the simultaneous reaction occurring along the schemes shown in Fig. 7. The reason why this branch reaction is possible in the case of alcoholic solvolysis must lie in the fact that the weak linkages in the intermediate IV are not restricted to the one diagonally opposite, because the ethyl radical is very large as compared with hydrogen atom and does not become ionized while hydrogen does. Other P–O–P linkages

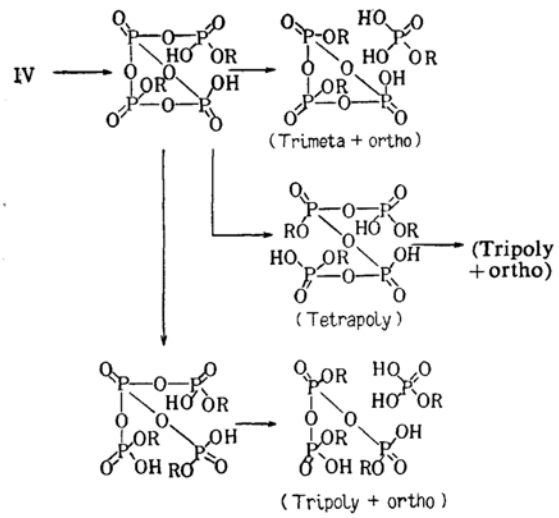


Fig. 7. Formulation of the process of tripoly-, tetrapoly- and orthophosphoric acid formation.

represented by sides of the square in IV may rupture though to a less extent. The phosphorus atom quota found in trimeta- and tripolyphosphoric acids and that found in orthophosphoric acid are in the ratio of three to one, which is quite consistent with the above-mentioned postulation.

When alcohol mixed with a small quantity of water is the reacting solvent against the oxide, tripoly- and trimetaphosphoric acids appear in a conspicuous amount in place of pyrophosphoric acid. As the water content further increases, these tri- species are very rapidly replaced by tetrametaphosphoric acid. It must, however, be noted that the above-mentioned transient increase in tripoly- and trimetaphosphoric acid is not accompanied by the production of a corresponding amount of orthophosphoric acid.

The branch reaction mentioned above does not explain the missing of orthophosphoric acid in this case, and for that same reason, it can explain the increase neither in tripoly- nor in trimetaphosphoric acid. These tri-species can not originate from highpolyphosphoric acid as precursor, because the production of the latter increases only gradually and without a maximum with the increase of water content in the solvent.

Involvement of condensation mechanism of phosphate radicals is the only conceivable explanation for the above. Condensation of phosphate radicals is an endothermic reaction, and does not occur under usual conditions in solution. It is here postulated that it does occur when a solvolytic opening of the P–O–P

linkages gives rise to the excitation of phosphate radicals and when they are close to one another. The same argument will explain the ever increasing formation of highpolyphosphoric acid in hydrolysis. The maximum yield of tripoly- and trimetaphosphoric acid with 90% ethanol may be attributable to the condensation between a pyrophosphoric acid radical and free orthophosphate radical.

Vigorous reaction between the oxide and water evolves much heat, and even under a cooling condition, some local heating can not be avoided. This must undoubtedly promote the condensation process.

Thorough dispersion of the oxide in dry ether or benzene was attempted to ensure synchronized contact with a large amount of water. Similar experiments, using ether and benzene containing trace quantities of water were carried out as well. In the former case, one would expect complete transformation to 100% tetrametaphosphoric acid, whereas in the latter case, one would expect 100% highpolyphosphoric acid. Difficulty in pulverizing the oxide crystals and the reacted mass prevented us from obtaining clear-cut results, but the expected tendency was observed.

Acetone may behave as a solvent having -OH radicals, as is explicable by its enol form, forming $-P-O-C\diagdown^{CH_3}_{CH_2}$ on solvolytic opening of a P-O-P linkage. This must be an intermediate very liable to undergo subsequent decomposition giving rise to a fairly large amount of highpolyphosphoric acid as the final hydrolysis product. Tetrametaphosphoric acid can be detected right from the beginning of the reaction, as well as tripoly- and trimetaphosphoric acid. In this case too, almost no orthophosphoric acid is produced.

Orthophosphoric acid is the most easily detectable species among various phosphates; it is inconceivable for us to have missed it in the analysis.

## Summary

1. α-Phosphorus(V) oxide was allowed to react with water, with ethanol or acetone, both dry or mixed with water by adding the powder crystal directly into these liquids. The oxide was also brought in contact with water after being dispersed in diethyl ether or benzene mechanically.

2. The main final hydrolysis products formed in the following cases were tetrametaphosphoric acid by direct action of a large quantity of water, pyrophosphoric acid by anhydrous ethanol, tripolyphosphoric acid by ethanol with a low water content, and highpolyphosphoric acid by anhydrous acetone. Quick contact with water after the oxide has been dispersed in ether or benzene leads to the formation of a larger amount of tetrametaphosphoric acid when these solvents were dry, while the formation of an increased amount of highpolyphosphoric acid was the result when they contained trace quantities of water initially.

3. Separation, identification and estimation of various condensed phosphate species were executed by paper chromatography and colorimetric analysis.

4. Reaction mechanisms were postulated to explain these results. Special attention was given to the solvolytic opening of P-O-P linkages and the accompanying condensation process of phosphate radicals.

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