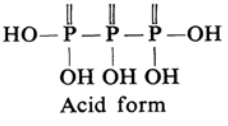
The Ultraviolet Absorption Spectra and the Hydrolysis of $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}$*-Acid*[1]

By Norimasa YOZA and Shigeru OHASHI

(Received July 15, 1963)

It is well known that the popular and fundamental oxo acids of phosphorus, i. e., hypophosphorous, phosphorous, hypophosphoric, orthophosphoric, and condensed phosphoric acid, do not show any remarkable absorption in the ultraviolet wavelength region of 220～400 mμ. However, in the course of a systematic spectrophotometric study of the oxo acids of phosphorus, the authors found that some of the compounds which contain P–P linkages exhibit absorption spectra in that ultraviolet region. One of them is the oxo acid of phosphorus with lower oxidation numbers, which has the following structural formula and which is represented by the abbreviated formula indicated below (A chemical name has not yet been given to this acid):



$$\mathrm{HO}-\underset{\mathrm{OH}}{\overset{\mathrm{O}}{\mathrm{P}}}-\underset{\mathrm{OH}}{\overset{\mathrm{O}}{\mathrm{P}}}-\underset{\mathrm{OH}}{\overset{\mathrm{O}}{\mathrm{P}}}-\mathrm{OH}$$

Acid form

$$\overset{4}{\mathrm{P}}-\overset{3}{\mathrm{P}}-\overset{4}{\mathrm{P}}$$

Abbreviated formula

The present investigation revealed that the absorption spectra of the $\overset{4}{\mathrm{P}}-\overset{3}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-acid vary remarkably with the pH of the solution and that this variation of the spectra can be explained in connection with a pH titration curve of this acid reported by Blaser and Worms.[2]

Blaser and Worms performed the hydrolysis of the $\overset{4}{\mathrm{P}}-\overset{3}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-acid in nitric acid solutions; its rates were measured by means of iodometric and bromometric titrations. In the present investigation, the hydrolysis of this acid was carried out in perchloric acid solutions in order to minimize the hindrance arising from the complex formation between an acid as a medium and metal ions, a formation of which will be encountered in a future study concerning the effect of the metal ions on the hydrolysis of the $\overset{4}{\mathrm{P}}-\overset{3}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-acid. The rates of its hydrolysis were readily determined by the ultraviolet spectrophotometric method. By the present investigation it was found that the rate constant of the hydrolysis of the $\overset{4}{\mathrm{P}}-\overset{3}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-acid increases linearly with the activity of perchloric acid.

Experimental

Materials.—The salts* of $\overset{1}{\mathrm{P}}$-, $\overset{3}{\mathrm{P}}$-, $\overset{5}{\mathrm{P}}$-, and $\overset{5}{\mathrm{P}}$-O-$\overset{5}{\mathrm{P}}$-acid were commercial reagents, while the salts* of $\overset{3}{\mathrm{P}}$-O-$\overset{3}{\mathrm{P}}$, $\overset{2}{\mathrm{P}}$-$\overset{4}{\mathrm{P}}$-, (-$\overset{3}{\mathrm{P}}$-)$_6$-ring, $\overset{3}{\mathrm{P}}$-O-$\overset{4}{\mathrm{P}}$-$\overset{4}{\mathrm{P}}$-, $\overset{4}{\mathrm{P}}$-$\overset{3}{\mathrm{P}}$-$\overset{4}{\mathrm{P}}$-, $\overset{3}{\mathrm{P}}$-O-$\overset{5}{\mathrm{P}}$-, $\overset{4}{\mathrm{P}}$-$\overset{4}{\mathrm{P}}$-, (-$\overset{4}{\mathrm{P}}$-$\overset{4}{\mathrm{P}}$-O-)$_2$-ring, $\overset{4}{\mathrm{P}}$-$\overset{4}{\mathrm{P}}$-O-$\overset{4}{\mathrm{P}}$-$\overset{4}{\mathrm{P}}$-, and $\overset{5}{\mathrm{P}}$-O-$\overset{4}{\mathrm{P}}$-$\overset{4}{\mathrm{P}}$-acid were supplied by Blaser and Worms.

Buffer Solutions. — The pH of the solutions was adjusted with perchloric acid, citric acid, sodium acetate, sodium monohydrogen orthophosphate, sodium dihydrogen orthophosphate, sodium tetraborate decahydrate, sodium carbonate, and sodium hydroxide.[3]

---

[1] Abbreviated formulas of this kind have been proposed by Blaser and Worms. The Arabic numerals attached to the phosphorus atoms represent their oxidation numbers. See B. Blaser and K.-H. Worms, *Z. anorg. u. allgem. Chem.*, **300**, 225 (1959).

[2] B. Blaser and K.-H. Worms, ibid., **300**, 250 (1959).

* The chemical formulas of these salts were shown in a previous paper; cf. Ref. 4.

[3] R. A. Robinson, "The Structure of Electrolytic Solutions," John Wiley & Sons Inc., New York (1959), p. 253.

The Measurement of Absorbances. — The measurement of absorbances was carried out with a Shimadzu photoelectric spectrophotometer QB-50 with 1.00 cm. silica cells. In order to keep the cell temperature constant, water of a constant temperature was circulated into a cell mount.

The Determination of the Rate Constants. — Hydrolytic reactions were started by mixing perchloric acid solutions and sample solutions, both of which had been preequilibrated thermally in a constant-temperature bath. The rate constants were calculated from the data obtained by measuring the decrease of the absorbances at 215 mμ with time.

Paper Chromatography and Colorimetry.—The ascending technique was employed for paper chromatographic identification[4] of reaction products. $\overset{3}{\mathrm{P}}$– and $\overset{4}{\mathrm{P}}$–$\overset{4}{\mathrm{P}}$–acid were determined colorimetrically with a molybdenum(V)-molybdenum(VI) reagent.[5]

Results and Discussion

There have been no studies of the ultraviolet absorption spectra of oxo acids of phosphorus, especially of the lower oxo acids of phosphorus, which have been recently discovered. Therefore, it was first tested whether any of the oxo acids of phosphorus in aqueous solutions give absorption spectra in the ultraviolet region of 220∼400 mμ. It was verified that, of $\overset{1}{\mathrm{P}}$–, $\overset{3}{\mathrm{P}}$–, $\overset{3}{\mathrm{P}}$–O–$\overset{3}{\mathrm{P}}$–, $\overset{2}{\mathrm{P}}$–$\overset{4}{\mathrm{P}}$–, $\overset{3}{\mathrm{P}}$–O–$\overset{4}{\mathrm{P}}$–$\overset{4}{\mathrm{P}}$–, $\overset{3}{\mathrm{P}}$–O–$\overset{5}{\mathrm{P}}$–, $\overset{4}{\mathrm{P}}$–$\overset{4}{\mathrm{P}}$–, (–$\overset{4}{\mathrm{P}}$–$\overset{4}{\mathrm{P}}$–O–)$_2$–ring, $\overset{4}{\mathrm{P}}$–$\overset{4}{\mathrm{P}}$–O–$\overset{4}{\mathrm{P}}$–$\overset{4}{\mathrm{P}}$–, $\overset{5}{\mathrm{P}}$–O–$\overset{4}{\mathrm{P}}$–$\overset{4}{\mathrm{P}}$–, $\overset{5}{\mathrm{P}}$–, and $\overset{5}{\mathrm{P}}$–O–$\overset{5}{\mathrm{P}}$–acid in aqueous solutions none afford any ultraviolet absorption spectra. However, it was found that $\overset{4}{\mathrm{P}}$–$\overset{3}{\mathrm{P}}$–$\overset{4}{\mathrm{P}}$– and (–$\overset{3}{\mathrm{P}}$–)$_6$– ring acid in aqueous solutions show characteristic absorption spectra in the ultraviolet region. It may be possible to analyze the $\overset{4}{\mathrm{P}}$–$\overset{3}{\mathrm{P}}$–$\overset{4}{\mathrm{P}}$– or (–$\overset{3}{\mathrm{P}}$–)$_6$–ring acid quantitatively or qualitatively in the presence of other oxo acids of phosphorus by means of the ultraviolet absorption spectra. It is interesting to note that both of these acids have more than two P–P linkages in their structures.

In this paper only the absorption spectra of the $\overset{4}{\mathrm{P}}$–$\overset{3}{\mathrm{P}}$–$\overset{4}{\mathrm{P}}$–acid will be discussed. As for the (–$\overset{3}{\mathrm{P}}$–)$_6$–ring acid, there are two maxima at 206 and 221 mμ in its absorption spectrum when the pH of the solution is 6.7. For the complete explanation of the absorption spectra of this acid, however, further investigation is required.

The Absorption Spectra of $\overset{4}{\mathrm{P}}$–$\overset{3}{\mathrm{P}}$–$\overset{4}{\mathrm{P}}$–Acid.—The absorption spectra of the $\overset{4}{\mathrm{P}}$–$\overset{3}{\mathrm{P}}$–$\overset{4}{\mathrm{P}}$–acid were measured at various pH values. As Figs. 1 and 2 show, the shapes of the absorption spectra vary remarkably with the pH change of the solutions.

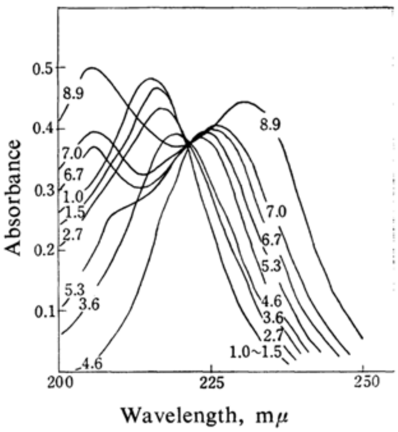


Fig. 1. pH dependence of the absorption spectra of $\overset{4}{\mathrm{P}}$–$\overset{3}{\mathrm{P}}$–$\overset{4}{\mathrm{P}}$–acid (1.54×10^{-4} M) in aqueous solutions (pH 1.0∼8.9).

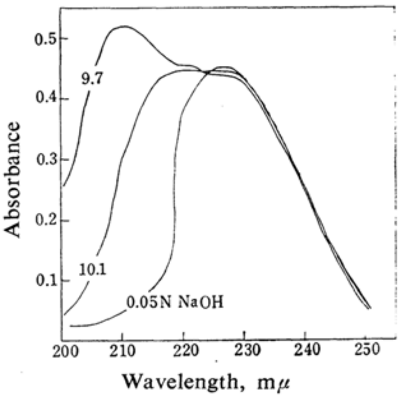


Fig. 2. pH dependence of the absorption spectra of $\overset{4}{\mathrm{P}}$–$\overset{3}{\mathrm{P}}$–$\overset{4}{\mathrm{P}}$–acid (1.54×10^{-4} M) in aqueous solutions (pH 9.7—0.05 N NaOH).

In an alkaline solution with a pH higher than 11, the spectrum exhibit the maximum absorption at the wavelength of 226 mμ. With the decreasing pH of the solution, the absorbance in the range of the shorter wavelengths increases. Thus, for instance, the absorption spectrum taken at pH 8.9 has two maxima at 205 and 230 mμ. With a further decrease of pH, the peak at 205 mμ diminishes, the maximum at 230 mμ shifts towards the shorter wavelength, and at last the absorption spectrum with only one peak appears. For example, at pH 4.6 one can observe a spectrum with its maximum at 224 mμ only.

When the pH of the solution decreases further, the maximum shifts more and more towards the shorter wavelength side while, at

---

[4] S. Ohashi and N. Yoza, This Bulletin, 36, 707 (1963).

[5] N. Yoza and S. Ohashi, report presented at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

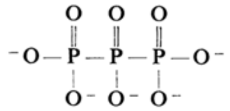
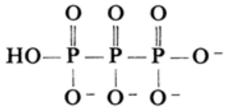
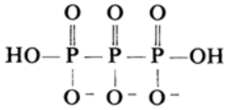
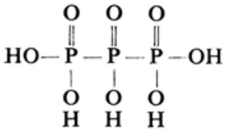
the same time, its absorbance increases. At pH 1 the spectrum indicates a maximum at 215 mμ. In the range of pH lower than 1, the absorption maximum at 215 mμ is always observed. However, in this range, the $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}$-acid is unstable, and the intensity of the absorbance decreases with time.

There have been reports on the pH dependence of the absorption spectra of some dibasic acids, such as sulfurous acid.3) In these cases the variations of the absorption spectra with the pH value have been attributed to the transformation between ionized and unionized species of the molecule in question.

As for $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}$-acid, an analogous discussion is possible in comparison with the pH titration data for this acid. The pH titration curve2) of $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}$ acid exhibits three inflection points at pH values, ca. 11, 9 and 5, corresponding to $P_3O_8^{5-}$, $HP_3O_8^{4-}$ and $H_2P_3O_8^{3-}$ respectively.

It is reasonable to assign the characteristic ultraviolet absorption spectra of $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}$-acid to three successively ionized species, $P_3O_8^{5-}$, $HP_3O_8^{4-}$, and $H_2P_3O_8^{3-}$, and to one unionized species, $H_5P_3O_8$, as indicated in Table I. The peak at 226 mμ is attributed to the negatively-charged anion formed by the removal of five protons from the unionized molecule, while the spectrum with the maxima at 205 and 230 mμ is assigned to the unsymmetrical species with four negative charges. Similarly, the spectrum with the maximum at 224 mμ is ascribed to the species with three negative charges, and the spectrum with the maximum at 215 mμ, to the unionized species of $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}$-acid.

TABLE I. RELATION BETWEEN THE ULTRAVIOLET ABSORPTION SPECTRA OF THE $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}$-ACID AND pH OF THE SOLUTIONS

Species	Stability	Maximum of the spectrum mμ	pH of the solution
 $^{-}O-\overset{\overset{O}{\|}}{\underset{\underset{O^-}{\mid}}{P}}-\overset{\overset{O}{\|}}{\underset{\underset{O^-}{\mid}}{P}}-\overset{\overset{O}{\|}}{\underset{\underset{O^-}{\mid}}{P}}-O^-$	Stable	226	11
 $HO-\overset{\overset{O}{\|}}{\underset{\underset{O^-}{\mid}}{P}}-\overset{\overset{O}{\|}}{\underset{\underset{O^-}{\mid}}{P}}-\overset{\overset{O}{\|}}{\underset{\underset{O^-}{\mid}}{P}}-O^-$	Stable	205 230	9
 $HO-\overset{\overset{O}{\|}}{\underset{\underset{O^-}{\mid}}{P}}-\overset{\overset{O}{\|}}{\underset{\underset{O^-}{\mid}}{P}}-\overset{\overset{O}{\|}}{\underset{\underset{O^-}{\mid}}{P}}-OH$	Stable	224	5
 $HO-\overset{\overset{O}{\|}}{\underset{\underset{OH}{\mid}}{P}}-\overset{\overset{O}{\|}}{\underset{\underset{OH}{\mid}}{P}}-\overset{\overset{O}{\|}}{\underset{\underset{OH}{\mid}}{P}}-OH$	Unstable (hydrolysis)	215	1

The Hydrolytic Decomposition of $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}$-Acid.—The rate of the hydrolysis of $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}$-acid is quite slow in a solution of low acidity, but it is catalytically accelerated by the addition of acid. It was confirmed by Blaser and Worms2) that the hydrolysis of $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}$-acid in 1.5 N nitric acid proceeds by the following two paths;

$$\overset{4}{P}-\overset{3}{P}-\overset{4}{P}\text{-Acid} \rightarrow \overset{3}{P}\text{-Acid} + \overset{4}{P}-\overset{4}{P}\text{-Acid} \qquad \text{(A)}$$

$$\overset{4}{P}-\overset{3}{P}-\overset{4}{P}\text{-Acid} \rightarrow \overset{5}{P}\text{-Acid} + \overset{2}{P}-\overset{4}{P}\text{-Acid}$$

$$\rightarrow \overset{5}{P}\text{-Acid} + 2\overset{3}{P}\text{-Acid} \qquad \text{(B)}$$

TABLE II. RATE CONSTANTS OF THE HYDROLYSIS OF THE $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}$-ACID IN PERCHLORIC ACID SOLUTIONS OF VARIOUS CONCENTRATIONS (measured at 215 mμ and 30.4°C)

No.	Concentrations of perchloric acid, N	Rate constants, min^{-1}
1	0.240	6.98×10^{-4}
2	0.480	1.73×10^{-3}
3	0.720	2.50×10^{-3}
4	0.960	3.30×10^{-3}
5	1.20	4.07×10^{-3}
6	1.44	4.90×10^{-3}
7	1.68	7.16×10^{-3}
8	1.92	8.92×10^{-3}
9	2.16	1.04×10^{-2}
10	2.40	1.34×10^{-2}
11	2.64	1.61×10^{-2}
12	2.88	1.88×10^{-2}

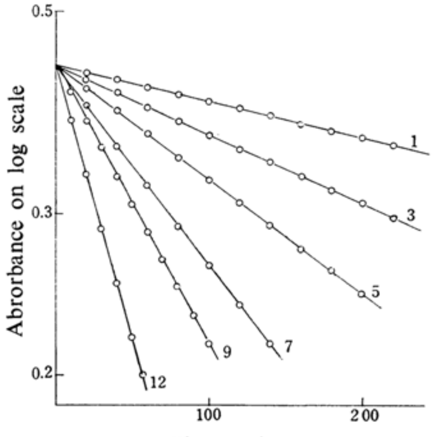
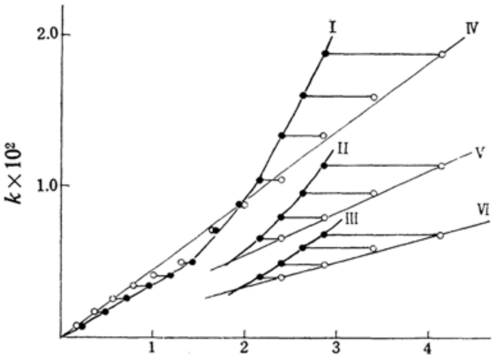


Fig. 3. The hydrolysis of $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}$-acid ($1.64\times10^{-4}$ M) in perchloric acid.
The numbers in this figure correspond to the numbers in Table II.



Normality or activity of perchloric acid

Fig. 4. Relationship between the rate constant, k, of the hydrolysis of $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}$-acid and the concentration of perchloric acid.
I, II and III; k vs. normality at 30.4, 25.0 and 20.0°C
IV, V and VI; k vs. activity at 30.4, 25.0 and 20.0°C

and that 82% of the $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}$-acid is decomposed by Path A and 18% of it by Path B.

However, it was found by the present investigation, paper chromatographically and colorimetrically, that equimolar amounts of $\overset{3}{P}$ and $\overset{4}{P}-\overset{4}{P}$-acid are produced by the hydrolysis of the $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}$-acid in perchloric acid solutions. Therefore, it was concluded that the hydrolysis of the $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}$-acid in perchloric acid solutions proceeds only by Path A. The difference between the reaction mechanisms for the hydrolysis of the $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}$-acid in nitric acid and in perchloric acid solutions can not be explained at the present state of knowledge.

The decrease in the concentration of $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}$-acid by hydrolysis can be readily pursued by measuring the absorbances at 215 mμ due to the unionized species of this acid, because the hydrolysis products, $\overset{3}{P}$- and $\overset{4}{P}-\overset{4}{P}$- acid, do not show any absorption. As shown in Fig. 3, the hydrolysis of $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}$-acid follows the first order rate law. Thus, the rate constant, k, is calculated from the equation:

$$k=\{2.303/(t_2-t_1)\}\log(E_1/E_2)$$

where E_1 and E_2 represent the absorbances at 215 mμ measured at the times t_1 and t_2 respectively. The rate constants obtained for the disappearance of the $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}$-acid in the perchloric acid solutions of various concentrations at 30.4°C are presented in Table II, from which it can be seen that the rate constant increases considerably with the increase in the acidity.

In Fig. 4, the rate constants measured at 30.4, 25.0 and 20.0°C are plotted against the normalities and activities of perchloric acid. Since there are not sufficient data on the activity coefficients of perchloric acid, some of them have been obtained graphically by interpolation from the known data[6] for 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, and 3.0 N perchloric acid. It can be concluded that there is a linear relationship between the rate constant of the hydrolysis of the $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}$-acid and the activity of perchloric acid.

Activation Energy.—From the rate constants measured at three different temperatures, one can estimate the activation energy for the hydrolysis of $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}$-acid to be 16.6 kcal. per mol. This value is considerably smaller than that for the hydrolysis at the P–P linkage of hypophosphoric acid, 20∼25 kcal. per mol.[7]

Summary

It has been found that $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}$-acid in aqueous solutions shows characteristic ultraviolet absorption spectra, which vary remarkably with the pH change of the solutions. The spectra having absorption maxima at 226, both 205 and 230, 224, and 215 mμ can be assigned to $P_3O_8^{5-}$, $HP_3O_8^{4-}$, $H_2P_3O_8^{3-}$, and $H_5P_3O_8$ respectively.

The rates of the hydrolysis of the $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}$-acid in the perchloric acid solutions have been determined by measuring the absorbance at 215 mμ. The hydrolysis follows the first order rate law. The hydrolysis products are $\overset{3}{P}$- and $\overset{4}{P}-\overset{4}{P}$-acid. The rate constant is in the linear function with the activity of perchloric acid. The activation energy has been estimated to be 16.6 kcal. per mol.

The authors wish to express their hearty thanks to Professor Jun Yoshimura for his kind suggestions made in the course of this work. The authors also wish to thank Dr. Bruno Blaser and Dr. Karl-Heinz Worms for supplying the samples used in this study.

Department of Chemistry
Faculty of Science
Kyushu University
Hakozaki, Fukuoka

---

[6] "Handbook of Analytical Chemistry," McGraw-Hill Book Company Inc., New York (1963), p. 10.

[7] J. R. Van Wazer, "Phosphorus and its Compounds," Interscience Publishers, New York (1958), p. 411.