The Reactions of Lower Oxo Acids of Phosphorus with the Molybdenum(V)-Molybdenum(VI) Reagent

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In a previous paper[1] it has been found that hypophosphoric acid reacts with the molybdenum(V)-molybdenum(VI) reagent to form a blue complex, while hypophosphorous and phosphorous acid do not produce any color reactions. Orthophosphoric acid also reacts with this reagent to form a blue complex, as has been pointed out by Lucena-Conde and Prat.[2] The blue complexes due to hypophosphoric and orthophosphoric acid are called "hypophosphoric heteropoly blue" and "orthophosphoric heteropoly blue" respectively.[1] The present investigation deals with the color reactions of various lower oxo acids of phosphorus with this reagent. The data obtained indicate that the mechanism of these reactions are closely related to the structural units of the lower oxo acids of phosphorus and their hydrolysis reactions. The abbreviated notations proposed by Blaser and Worms[3] will be used for the oxo acids of phosphorus in this paper. For instance, hypophosphorous, phosphorous, hypophosphoric, and orthophosphoric acid are represented by the notations, $\overset{1}{\mathrm{P}}$–, $\overset{3}{\mathrm{P}}$–, $\overset{4}{\mathrm{P}}$–$\overset{4}{\mathrm{P}}$–, and $\overset{5}{\mathrm{P}}$–acid respectively. The Arabic numerals attached to the phosphorus atoms represent the oxidation numbers of the phosphorus atoms.

Experimental

Reagent. — All the reagents used in this work have been described in previous papers.[1,4]

The Procedure for the Color Reactions. — A suitable aliquot of a neutral solution of a given sample (about 10^{-4} M) was taken in a 25 ml. volumetric flask, diluted to approximately 20 ml. with water, and treated by each of the following three procedures. After the volume of the solution had been adjusted to the mark with water, the absorption spectrum was measured by the use of a Shimadzu photoelectric spectrophotometer, QB-50, with 1 cm. cells.

Procedure I. — The sample solution was allowed to react with 2 ml. of the molybdenum(V)-molybdenum(VI) reagent for 30 min. at room temperature.

Procedure II. — The sample solution was allowed to react with 2 ml. of the molybdenum(V)-molybdenum(VI) reagent for 1 hr. at 95°C.

Procedure III. — The sample solution was allowed to react with a mixture of 1 ml. of 1 M sodium hydrogen sulfite solution and 2 ml. of the molybdenum(V)-molybdenum(VI) reagent for 1 hr. at 95°C.

Results and Discussion

As has been pointed out in a previous

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[1] N. Yoza and S. Ohashi, This Bulletin, **37**, 33 (1964).

[2] F. Lucena-Conde and L. Prat, *Anal. Chim. Acta*, **16**, 473 (1957).

[3] B. Blaser and K.-H. Worms, *Z. anorg. u. allgem. Chem.*, **300**, 225 (1959)

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

paper,[1] $\overset{4}{P}$–$\overset{4}{P}$–acid reacts with the molybdenum(V)-molybdenum(VI) reagent under the conditions of procedures I and II to form hypophosphoric heteropoly blue, the absorption spectrum of which has two maxima, at 590 and 670 mμ, while $\overset{1}{P}$– and $\overset{3}{P}$–acid do not give any colored products under the conditions of either procedures I or II. $\overset{5}{P}$–Acid reacts with this reagent under the conditions of procedure II to form orthophosphoric heteropoly blue, the absorption spectrum of which has a maximum at 820 mμ. Under the conditions of procedure I, the rate of the reaction is so slow that $\overset{5}{P}$–acid gives only a faint blue color. If the quantity of $\overset{5}{P}$–acid is comparable to that of $\overset{4}{P}$–$\overset{4}{P}$–acid, the absorbance due to orthophosphoric heteropoly blue is negligibly small compared with that due to hypophosphoric heteropoly blue.

In the course of this investigation, it was found that $\overset{1}{P}$– or $\overset{3}{P}$–acid is quantitatively oxidized with sodium hydrogen sulfite to $\overset{5}{P}$–acid when heated in an acid solution at 95°C. The sulfite is reduced to elemental sulfur in the course of this reaction. Therefore, when $\overset{1}{P}$– or $\overset{3}{P}$–acid is treated by procedure III, orthophosphoric heteropoly blue is produced quantitatively. Since the elemental sulfur produced coagulates, it does not interfere with the measurement of the absorbance of the blue color.

The reactions of twelve lower oxo acids of phosphorus as well as of $\overset{5}{P}$–acid with the molybdenum(V)-molybdenum(VI) reagent were carried out by procedures I, II, and III. All the blue products were either orthophosphoric or hypophosphoric heteropoly blue, or a mixture of them. The quantities of both the heteropoly blues were calculated from the absorbances of the spectra. All the results are summarized in Table I. The final acidity of the reaction mixture is approximately 1 N with respect to the sulfuric and hydrochloric acid in all cases.[1] Since the molecular structures of orthophosphoric and hypophosphoric heteropoly blue have not been determined, it is assumed, for the sake of convenience, that one mole of each heteropoly blue contains one mole of $\overset{5}{P}$– or $\overset{4}{P}$–$\overset{4}{P}$– units.

The Reactions with Procedure I. — One mole of $\overset{3}{P}$–O–$\overset{4}{P}$–$\overset{4}{P}$–, $(-\overset{4}{P}-\overset{4}{P}-O-)_2$–ring, $\overset{4}{P}$–$\overset{4}{P}$–O–$\overset{4}{P}$–$\overset{4}{P}$–, or $\overset{5}{P}$–O–$\overset{4}{P}$–$\overset{4}{P}$–acid, which contains one or two

TABLE I. THE PRODUCTS OBTAINED BY THE REACTIONS OF OXO ACIDS OF PHOSPHORUS WITH THE MOLYBDENUM(V)-MOLYBDENUM(VI) REAGENT

Oxo acid of phosphorus (starting compd.)	Procedure I		Procedure II		Procedure III	
	$\overset{4}{P}$-$\overset{4}{P}$-Mo	$\overset{5}{P}$-Mo	$\overset{4}{P}$-$\overset{4}{P}$-Mo	$\overset{5}{P}$-Mo	$\overset{4}{P}$-$\overset{4}{P}$-Mo	$\overset{5}{P}$-Mo
$\overset{1}{P}$-Acid	0	0	0	0	0	1.04
$\overset{3}{P}$-Acid	0	0	0	0	0	1.01
$\overset{3}{P}$-O-$\overset{3}{P}$-Acid	0	0	0	0	0	1.96
$\overset{2}{P}$-$\overset{4}{P}$-Acid	0	0	0	0	<0.2	1.94
$(-\overset{3}{P}-)_6$-Ring acid	0.81	0	0.81	0	1.26±0.1	3.28±0.2
$\overset{3}{P}$-O-$\overset{4}{P}$-$\overset{4}{P}$-Acid	1.05	0	1.04	0	1.04	1.03
$\overset{4}{P}$-$\overset{3}{P}$-$\overset{4}{P}$-Acid	1.00	0	1.02	0	1.02	0.99
$\overset{3}{P}$-O-$\overset{5}{P}$-Acid	0	0	0	1.03	0	2.01
$\overset{4}{P}$-$\overset{4}{P}$-Acid	1.00	0	1.00	0	1.01	0
$(-\overset{4}{P}-\overset{4}{P}-O-)_2$-Ring acid	2.06	0	2.03	0	2.07	0
$\overset{4}{P}$-$\overset{4}{P}$-O-$\overset{4}{P}$-$\overset{4}{P}$-Acid	1.89	0	1.91	0	1.93	0
$\overset{5}{P}$-O-$\overset{4}{P}$-$\overset{4}{P}$-Acid	0.98	0	0.98	0.98	0.98	0.98
$\overset{5}{P}$-Acid	0	0	0	1.01	0	1.00

Mole ratios of the products to the starting compounds are shown.

$\overset{4}{P}$-$\overset{4}{P}$-Mo; Hypophosphoric heteropoly blue

$\overset{5}{P}$-Mo; Orthophosphoric heteropoly blue

$\overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-units in its structure, produces one or two moles of hypophosphoric heteropoly blue when procedure I is used. These results suggest that all the four oxo acids undergo hydrolysis to form $\overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-acid, which reacts successively with the molybdenum(V)-molybdenum(VI) reagent. One mole of $\overset{4}{\mathrm{P}}-\overset{3}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-acid produces one mole of hypophosphoric heteropoly blue. Therefore, it is evident that $\overset{4}{\mathrm{P}}-\overset{3}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-acid is hydrrolyzed by procedure I according to Eq. 1, not Eq. 2:

$$\overset{4}{\mathrm{P}}-\overset{3}{\mathrm{P}}-\overset{4}{\mathrm{P}}\text{-Acid} \rightarrow \overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}\text{-Acid} + \overset{3}{\mathrm{P}}\text{-Acid} \qquad (1)$$

$$\begin{aligned}\overset{4}{\mathrm{P}}-\overset{3}{\mathrm{P}}-\overset{4}{\mathrm{P}}\text{-Acid} &\rightarrow \overset{2}{\mathrm{P}}-\overset{4}{\mathrm{P}}\text{-Acid} + \overset{5}{\mathrm{P}}\text{-Acid}\\ &\rightarrow 2\overset{3}{\mathrm{P}}\text{-Acid} + \overset{5}{\mathrm{P}}\text{-Acid} \qquad (2)\end{aligned}$$

As has been discussed in a previous paper,[5] $\overset{4}{\mathrm{P}}-\overset{3}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-acid is hydrolyzed also in a perchloric acid solution according to Eq. 1. One mole of $(-\overset{3}{\mathrm{P}}-)_6$-ring acid produces approximately 0.8 mol. of hypophosphoric heteropoly blue. Although the reaction mechanism of the hydrolysis of $(-\overset{3}{\mathrm{P}}-)_6$-ring acid has not been clarified, the data obtained here indicate at least that $\overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-acid is one of the main intermediate products in the hydrolysis of $(-\overset{3}{\mathrm{P}}-)_6$-ring acid. $\overset{1}{\mathrm{P}}$-, $\overset{3}{\mathrm{P}}$-, $\overset{3}{\mathrm{P}}-\mathrm{O}-\overset{3}{\mathrm{P}}$-, $\overset{2}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-, $\overset{3}{\mathrm{P}}-\mathrm{O}-\overset{5}{\mathrm{P}}$-, and $\overset{5}{\mathrm{P}}$-acid do not give any colored products when procedure I is used, because of the impossibility of its producing $\overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-acid.

The Reactions Using Procedure II.—The final products in the hydrolysis of $\overset{3}{\mathrm{P}}-\mathrm{O}-\overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-, $\overset{4}{\mathrm{P}}-\overset{3}{\mathrm{P}}-\overset{4}{\mathrm{P}}$, $\overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-, $(-\overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}-\mathrm{O}-)_2$-ring, $\overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}-\mathrm{O}-\overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-, and $\overset{5}{\mathrm{P}}-\mathrm{O}-\overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-acid are $\overset{3}{\mathrm{P}}$- and $\overset{5}{\mathrm{P}}$-acid when they are boiled in mineral acid.[6,7] As for $(-\overset{3}{\mathrm{P}}-)_6$-ring acid, the final products in the hydrolysis with mineral acid are $\overset{1}{\mathrm{P}}$-, $\overset{3}{\mathrm{P}}$- and $\overset{5}{\mathrm{P}}$-acid.[8] However, when procedure II is used, $(-\overset{3}{\mathrm{P}}-)_6$-ring, $\overset{3}{\mathrm{P}}-\mathrm{O}-\overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-, $\overset{4}{\mathrm{P}}-\overset{3}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-, $(-\overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}-\mathrm{O}-)_2$-ring, and $\overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}-\mathrm{O}-\overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-acid give hypophosphoric heteropoly blue, the absorption spectra of which are quite identical with those of the blue products obtained from the respective compounds by procedure I. One mole of $\overset{5}{\mathrm{P}}-\mathrm{O}-\overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-acid produces a mixture of one mole of orthophosphoric heteropoly blue and one mole of hypophosphoric heteropoly blue when procedure II is used. These results indicate that $\overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-acid produced by the hydrolysis of the lower oxo acids of phosphorus mentioned above reacts preferentially with the molybdenum(V)-molybdenum(VI) reagent and that the resulting hypophosphoric heteropoly blue is remarkably stable under the conditions of procedure II.

One mole of $\overset{3}{\mathrm{P}}-\mathrm{O}-\overset{5}{\mathrm{P}}$-acid produces one mole of orthophosphoric heteropoly blue when procedure II is used, because $\overset{3}{\mathrm{P}}-\mathrm{O}-\overset{5}{\mathrm{P}}$-acid is hydrolyzed to form $\overset{3}{\mathrm{P}}$- and $\overset{5}{\mathrm{P}}$-acid. $\overset{1}{\mathrm{P}}$-, $\overset{3}{\mathrm{P}}$-, $\overset{3}{\mathrm{P}}-\mathrm{O}-\overset{3}{\mathrm{P}}$-, and $\overset{2}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-acid do not give any colored products when procedure II is used.

The Reaction Using Procedure III.—One mole of $\overset{3}{\mathrm{P}}-\mathrm{O}-\overset{3}{\mathrm{P}}$-acid produces two moles of orthophosphoric heteropoly blue when procedure III is used, because $\overset{3}{\mathrm{P}}-\mathrm{O}-\overset{3}{\mathrm{P}}$-acid is hydrolyzed in the course of procedure III to form $\overset{3}{\mathrm{P}}$-acid. When procedure III is used, $\overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-, $(-\overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}-\mathrm{O}-)_2$-ring, $\overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}-\mathrm{O}-\overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-, and $\overset{5}{\mathrm{P}}-\mathrm{O}-\overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-acid give the same products as in the case of procedure II, because there is no $\overset{1}{\mathrm{P}}$- or $\overset{3}{\mathrm{P}}$-acid in the hydrolysis products of these oxo acids. Since one mole of $\overset{3}{\mathrm{P}}-\mathrm{O}-\overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}$- or $\overset{4}{\mathrm{P}}-\overset{3}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-acid is converted into one mole of $\overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-acid and one mole of $\overset{3}{\mathrm{P}}$-acid in the first step of its hydrolysis, the reaction products of $\overset{3}{\mathrm{P}}-\mathrm{O}-\overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}$- or $\overset{4}{\mathrm{P}}-\overset{3}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-acid obtained by procedure III exhibit the absorption spectra due to an equimolar mixture of orthophosphoric and hypophosphoric heteropoly blue. One mole of $\overset{3}{\mathrm{P}}-\mathrm{O}-\overset{5}{\mathrm{P}}$-acid produces, of course, two moles of orthophosphoric heteropoly blue when procedure III is used. $\overset{2}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-Acid produces orthophosphoric heteropoly blue with a small amount of hypophosphoric heteropoly blue when procedure III is used. Since the hydrolysis product of $\overset{2}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-acid in mineral acid is $\overset{3}{\mathrm{P}}$-acid, it is reasonable that the main product obtained by procedure III is orthophosphoric heteropoly blue. The small amount of hypophosphoric heteropoly blue may be due to the redox

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[5] N. Yoza and S. Ohashi, ibid., **36**, 1485 (1963).

[6] J. R. Van Wazer, "Phosphorus and its Compounds," Interscience Publishers, Inc., New York (1958), pp. 345-418.

[7] B. Blaser and K.-H. Worms, *Z. anorg. u. allgem. Chem.*, **300**, 250 (1959); **301**, 7 (1959); **311**, 313 (1961).

[8] B. Blaser and K.-H. Worms, ibid., **300**, 237 (1959).

reaction between sulfite and $\overset{2}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-acid, where a part of the $\overset{2}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-acid is oxidized to $\overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-acid. One mole of $(-\overset{3}{\mathrm{P}}-)_6$-ring acid produces a mixture of orthophosphoric and hypophosphoric heteropoly blue when procedure III is used. The data indicate that the mechanism of the hydrolysis of $(-\overset{3}{\mathrm{P}}-)_6$-ring acid varies with small differences in the reaction conditions. The results obtained for $(-\overset{3}{\mathrm{P}}-)_6$-ring acid by using procedures II and III suggest that $\overset{5}{\mathrm{P}}$-acid, as one of the final products in the hydrolysis of $(-\overset{3}{\mathrm{P}}-)_6$-ring acid by the action of mineral acid, may be derived from $\overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-acid as one of the intermediate products. $(-\overset{3}{\mathrm{P}}-)_6$-Ring acid forms a larger quantity of hypophosphoric heteropoly blue when procedure III is used than when procedure III is used. This fact may suggest that certain intermediate products, e. g., $\overset{2}{\mathrm{P}}-\overset{4}{\mathrm{P}}-$ or $\overset{2}{\mathrm{P}}-\overset{3}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-acid (a hypothetical compound), in the process of the hydrolysis of this ring acid, are oxidized with sulfite to $\overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-acid or some other compounds that give $\overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}$-acid as the result of hydrolysis.

Summary

The reaction of twelve lower oxo acids of phosphorus and orthophosphoric acid with the molybdenum(V)-molybdenum(VI) reagent have been carried out under the conditions prescribed by three different procedures: (1) the reactions for 30 min. at room temperature, (2) the reactions for 1 hr. at 95°C, and (3) the reactions in the presence of sodium hydrogen sulfite for 1 hr. at 95°C. The absorption spectra of the reaction products have been measured. It has been found that the blue products obtained by these reactions are orthophosphoric heteropoly blue and/or hypophosphoric heteropoly blue in all cases and that mechanisms of these reactions are closely related to the structural units of the lower oxo acids of phosphorus and their hydrolysis reactions.

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