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# Synthesis of Phosphorous Acid and Its Derivatives Based on the Reaction of Elemental Phosphorus ($P_4$) and Aqueous Solution of Choline in the Presence of the Hydroxides of Earth Alkali Metals

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ABSTRACT: *A nonchloric method for the synthesis of phosphorous acid and barium and calcium phosphites is proposed, involving the reaction of elemental phosphorus ($P_4$) with aqueous barium and calcium hydroxides in the presence of quaternary ammonium base (choline). Conditions for the preparation of high-purity phosphorous acid based on the oxidation of the hypophosphite ion to the phosphite ion in a strong alkali medium were studied.* © 2008 Wiley Periodicals, Inc. Heteroatom Chem 19:517–519, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20472

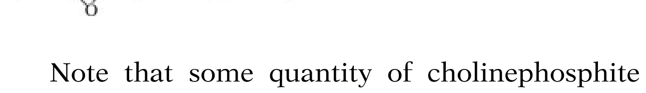
## INTRODUCTION

In recent years, we studied the reaction of elemental phosphorus ($P_4$) with proton donor reagents using bifunctional compounds, particularly metal complexes or amines, which appeared to promote the cleavage of the $P_4$ tetrahedron [1].

In connection with our research directed toward the development of new methods for the synthesis of phosphorus organic compounds, we have reported the synthesis of hypophosphite based on the reaction of elemental phosphorus with ethylene oxide in the presence of aqueous solution of tertiary amines [2].

## RESULTS AND DISCUSSION

We have established that the reaction of elemental phosphorus with choline and water is accompanied by the elimination of hydrogen ($H_2$), instead of phosphine, as it is usually performed when other tertiary amines were used [2]. Thus, the synthesis of choline-hypophosphite is described as shown below



Note that some quantity of cholinephosphite along with cholinehypophosphite is always formed in the above reaction. As it is known for the inorganic reactions [3,4], in the competition between the possible formation of hypophosphite and phosphite,

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the strong alkali medium is more favored than the formation of phosphite.

In connection with this, we studied the conditions for the preparation of phosphorous acid via the oxidation of the hypophosphite ion to the phosphite ion in a strong alkaline medium, particularly, 45%–50% solution of choline in the presence of earth alkali metal hydroxides $Ba(OH)_2$ or $Ca(OH)_2$, which promote the shifting of the reaction equilibrium toward the formation the respective metal phosphites. For the more full transformation of the hypophosphite ion into the phosphite ion, barium or calcium phosphites were removed from the reaction mixture as precipitate and then were decomposed with the excess of sulfuric acid. The following purification of phosphorous acid from the traces of sulfate ions with calculated quantity of the hydroxides of earth alkali metals resulted in phosphorous acid. At that time, the filtrate, which contains solution of choline, may be regenerated. The total process consists of the following principal stages:

$$P_4 + 8[(CH_3)_3N^+CH_2CH_2OH]OH^- + 4H_2O \rightarrow 4[(CH_3)_3N^+CH_2CH_2OH]_2^{2-}O_2P(O)H + 6H_2\uparrow$$

$$[(CH_3)_3N^+CH_2CH_2OH]_2^{2-}O_2P(O)H + H_2O + M(OH)_2 \rightarrow 2[(CH_3)_3N^+CH_2CH_2OH]OH^- + H_2 + MHPO_3\downarrow$$

$$MHPO_3 + H_2SO_4 \rightarrow H_3PO_3 + MSO_4\downarrow$$

$$(M = Ca \text{ or } Ba)$$

It should be noted that this method allows the preparation of a high purity phosphorous acid referring to the phosphorus (80%–90% yield).

Thus, the ecologically pure nonchloric method is proposed for the preparation of phosphorous acid based on the reaction of white phosphorus with hydroxide β-hydroxyethyltrimethylammonium (choline) in water in the presence of barium or calcium hydroxides.

## EXPERIMENTAL

The $^{31}P$ NMR spectra were recorded on a Bruker MSL-400 (162 MHz, external 85% phosphoric acid).

### Preparation of the Phosphorous Acid

(a) *Interaction of $P_4$, Trimethylamine, Ethylene Oxide, and Water in the Presence of Barium Hydroxide*. To a mixture of $P_4$ (5 g), trimethylamine (11.9 g), ethylene oxide (8.9 g), and water (14.5 g) at 40–45°C (mp of $P_4$), $Ba(OH)_2$ (70 g) was added, with the reagent molar ratio of 1:5:5:5.5:20. The reaction was conducted at 50–100°C up to the total conversion of phosphorus. After that, the formed $BaHPO_3$ was filtered off and washed with water (yield 28 g, 80%). The filtrate, containing β-hydroxyethyltrimethylammonium hydroxide (choline), may be recovered in the reaction. The precipitate of barium phosphite was added to a stirred 11%–12% solution of sulfuric acid (1.2–1.3 times excess of the stoichiometry) at 80–90°C. The formed $BaSO_4$ was filtered off and washed with water. The obtained 6%–7% solution of phosphorous acid was purified of traces of sulfate ions with $Ba(OH)_2$. The yield of phosphorous acid was 10.2 g (77%). $^{31}P$ NMR, $\delta = 3.2$, $^1J_{P\text{-}H} = 675$ Hz.

(b) *Interaction of $P_4$, β-Hydroxyethyltrimethylammonium Hydroxide, and Water in the Presence of Barium Hydroxide*. In a similar manner to that described for the preparation of phosphorous acid according to (a), from $P_4$ (5 g), β-hydroxyethyltrimethylammonium hydroxide (24.4 g), water (21.7 g), and $Ba(OH)_2$(70 g), being in the reagent molar ratio of 1:5:30:5.5, phosphorous acid (yield 10.4 g, 79%) was obtained.

(c) *Interaction of $P_4$, Trimethylamine, Ethylene Oxide, and Water in the Presence of Calcium Hydroxide*. To a mixture of $P_4$ (5 g), trimethylamine (11.9 g), ethylene oxide (8.9 g), and water (14.5 g) at 40–45°C (mp of $P_4$), $Ca(OH)_2$ (19.1 g) was added, with a reagent molar ratio of 1:5:5:30:6.5. The reaction was conducted in a strong alkali medium at 50–100°C until the total conversion of phosphorus. After that, the formed $CaHPO_3$ was filtered off and washed with water (yield 12.4 g, 64.1%). The precipitate of calcium phosphite was decomposed with 11%–12% solution of sulfuric acid (1.2–1.3 excess of the stoichiometry) at 80–90°C. The formed $CaSO_4$ was filtered off and washed with water. The obtained 5%–6% solution of phosphorous acid was purified from the traces of sulfate ions with $Ca(OH)_2$. The yield of phosphorous acid was 8.5 g (64.5 %). $^{31}$P NMR, $\delta = 3.2$, $^1J_{\text{P-H}} = 675$ Hz.

(d) *Interaction of $P_4$, β-Hydroxyethyltrimethylammonium Hydroxide, and Water in the Presence of Calcium Hydroxide*. In a similar manner to that described for the preparation of phosphorous acid according to (c), from $P_4$ (5 g), β-hydroxyethyltrimethylammonium hydroxide (24.4 g), water (21.7 g), and Ca $(OH)_2$ (19.1 g), with a reagent molar ratio of 1:5:30:6.5, the phosphorous acid (yield 8.9 g, 68%) was obtained.

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