Catalytic Method of Synthesis of Phosphorus Acids Esters from Zinc Phosphide and Alcohol

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Abstract—Ecologically safe effective catalytic method for preparing phosphorous and phosphoric acid esters by oxidation of zinc phosphide with oxygen in the solution of copper(II) halides in butanol at 50–70°C is developed. It is found that in the presence of Cu(II) chloride a mixture of dibutyl hydrogen phosphite and tributyl phosphate is formed, while at the catalysis with Cu(II) bromide tributyl phosphate is mainly obtained. Promoting action of hydrogen chloride on the reaction rate and yield of organophosphorus compounds is established. Optimal reaction conditions are found and redox mechanism of catalytic process is assumed.

Transition metal phosphides (Zn_3P_2, Cu_3P, FeP) possess valuable practical properties and are promising sources of new materials in various spheres of human activity, in particular, in medicine, biotechnology, and some other branches of industry. Such phosphides are comparatively cheap commercial products. Their production is based on reprocessing of phosphorite ores. Zinc phosphide (Zn_3P_2) is obtained in industry by the reaction of zinc dust with red phosphorus in a vacuum at 500°C. It is known as starting substance for the preparation of phosphine in the reactions of acidic hydrolysis and also for extermination of rodents. Metal phosphides exhibit high chemical stability to the action of mineral acids which complicates their reprocessing. One of the actual problems of chemistry and technology of phosphorus-containing materials (phosphides, alloys) is the development of highly effective methods of dephosphorization of metals. In the decomposition of materials containing phosphorus in the form of phosphides the presence of oxidizers is the necessary condition. In practice the reactions of acidic and alkaline decomposition are mainly used. Such reactions have very low rates and only in the presence of concentrated acids they can proceed quantitatively [1–3]. Low polar Zn_3P_2 molecule contains the fragments of P–P chains with covalent bonds. It is not practically used in synthesis of organophosphorus derivatives [4, 5].

We have found previously that $FeCl_3$ and the mixed $FeCl_3$–I_2 system are effective catalysts for oxidation of zinc phosphide with oxygen in butanol to tributyl phosphate and dibutyl hydrogen phosphite. Phosphorous and prosphoric acid esters are widely used in organic synthesis for the preparation of pharmaceuticals, biologically active substances, and as the extractants of rare and radioactive metals. They are also used as additives to lubricants and hydraulic liquids, and the inhibitors of polymer combustion and corrosion. Existing industrial manufacturing of these valuable organophosphorus compounds is the multi-stage process. It is based on using phosphorus chlorides and oxychlorides. In their turn these substances are prepared by chlorination of white phosphorus (P_4) [8].

Subsequent reactions of substitution of chlorine atoms with different functional groups are accompanied by formation of toxic difficultly utilizable chlorine-containing compounds.

With the purpose of broadening the range of catalysts of Zn_3P_2 oxidative decomposition with alcohol solutions we studied the activity of copper(II) halides, $CuBr_2$ and $CuCl_2$. The obtained results will favor the creation of principally new environmentally safe technologies for preparation of organophosphorus compounds under mild conditions.

It is found that in butanol solutions of $CuBr_2$ and $CuCl_2$ zinc phosphide at 50–70°C is oxidated with oxygen to dibutyl hydrogen phosphite **I** and tributyl phosphate **II** depending on the reaction conditions.
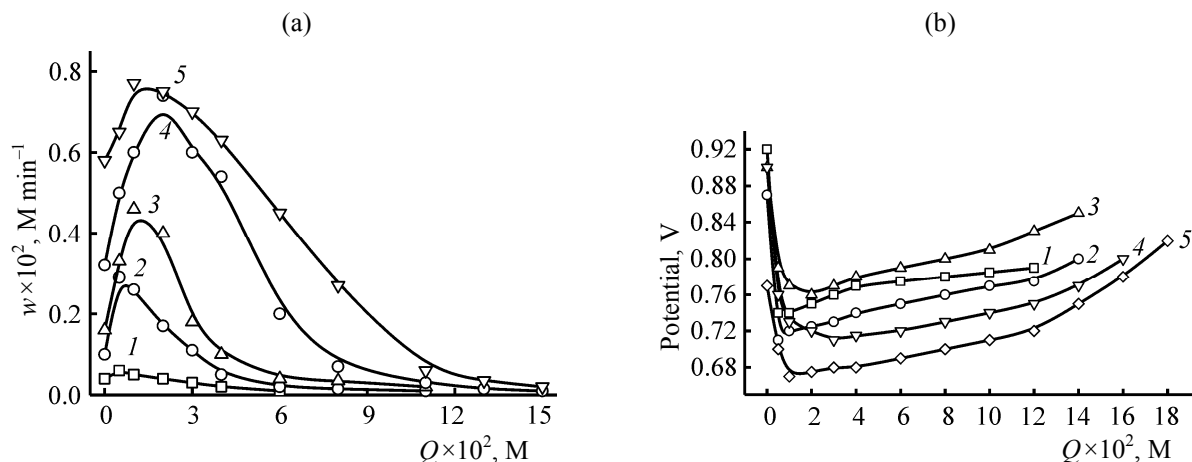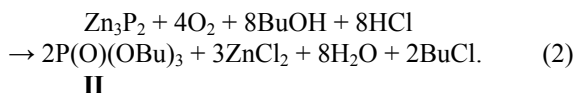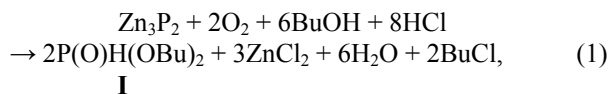
(a)

(b)

Fig. 1. (a) Conversion and (b) potentiometric curves of oxidation of zinc phosphide with oxygen in CuBr$_2$ butanol solution at different HCl concentrations. V(BuOH) 8 ml, V(PhMe) 2 ml, X(Zn$_3$P$_2$) 0.38 mmol; X(CuBr$_2$) 3.6 mmol; 70°C, P(O$_2$) 1 atm; X(HCl), mmol: (*1*) 0, (*2*) 3.1, (*3*) 3.7, (*4*) 6.1, and (*5*) 9.2.

$$Zn_3P_2 + 2O_2 + 6BuOH + 8HCl$$
$$\rightarrow 2P(O)H(OBu)_2 + 3ZnCl_2 + 6H_2O + 2BuCl, \qquad (1)$$
$$\textbf{I}$$

$$Zn_3P_2 + 4O_2 + 8BuOH + 8HCl$$
$$\rightarrow 2P(O)(OBu)_3 + 3ZnCl_2 + 8H_2O + 2BuCl. \qquad (2)$$
$$\textbf{II}$$

For the establishing of kinetics and mechanism of the process the effect of temperature, of the components of the reaction solution, and the nature of catalyst on the rate of the reactions (1), (2) and the yield of the products was studied.

CuBr$_2$ catalyst. Introduction of 0.38 mmol of zinc phosphide in the brown toluene-butanol solution of CuBr$_2$ at 70°C is accompanied by a color change to green, shifting of redox potential to the cathode side, and simultaneous absorption of oxygen. As is seen from Fig. 1 at the beginning of the experiment the rate of oxygen absorption is slow. Then it increases, passes through a maximum, and at the end of experiment it becomes close to zero. The amount of absorbed oxygen is close to stoichiometric. After the achievement of maximum the redox potential returns to the anode side approaching the initial value.

In the course of 6 h at the highest reaction rate 0.6×10^{-3} M min^{-1} 6.0×10^{-2} M of oxygen is absorbed to give 2% of dibutyl hydrogen phosphite **I** and 56% of tributyl phosphate **II** (Table 1, exp. 1). The reaction solution with the addition of 3.1 mmol HCl at the maximum rate 2.9×10^{-3} M min^{-1} absorbs 10^{-1} M of oxygen with the formation of 16% of compound **I** and 72% of substance **II** (exp. 2). The increase in HCl

amount to 6.1 mmol leads to significant increase in the reaction rate, in the amount of absorbed oxygen, and in the yield of organophosphorus compounds. Under these conditions a complete conversion of phosphide is observed. Yield of compound **I** is 18%, and of the product **II,** 82% (exps. 3, 4).

At the HCl concentration 9.2 mmol l^{-1} the rate of the reaction increases insignificantly, and the yield of organophosphorus compounds decreases to 55% (exp. 5). The decrease in CuBr$_2$/Zn$_3$P$_2$ ratio from 9.5 to 2.4 leads to the decrease in the yield of phosphate to 35% (exps. 4, 6–8). The decrease in temperature to 50°C to some extent decreases the rate of the process and the amount of absorbed oxygen, but the conversion of zinc phosphide remains high, and the preferred formation of phosphate **II** takes place (exps. 3, 9, 10). The decrease in the partial pressure of oxygen from 1 at to 0.2 at decreases the rate of O$_2$ absorption and the yield of organophosphorus compounds (exps. 3, 11, 12). In the absence of oxygen tributyl phosphate is also formed in 26% yield (exp. 13).

CuCl$_2$ catalyst. Analogous trends were found in the reaction of oxidative alkoxylation of Zn$_3$P$_2$ in butanol solution of CuCl$_2$ (Table 2). Unlike the system containing CuBr$_2$, the reaction rate and the amount of absorbed oxygen are higher, but under these conditions the conversion of Zn$_3$P$_2$ is 46–87%, and tributyl phosphate **II** and dibuthyl hydrogen phosphite **I** are formed in equal amounts. The increase in HCl (exps. 1–7) and CuCl$_2$ (exps. 5, 9, 10) concentrations at 70°C favors the increase in the yield of phosphate **II**. The decrease in temperature of the reaction mixture to 50°C

Table 1. Effect of concentration of CuBr$_2$ catalyst, of reagents and temperature on the rate of oxidation of Zn$_3$P$_2$ and yield of the products in butanol[a]

Exp. no.	x(CuBr$_2$), mmol (g)	x(Zn$_3$P$_2$), mmol (g)	x(HCl), mmol	w(O$_2$)×10^3, M min^{-1}	Q(O$_2$)×10^2, M	Yield, %	
						I	II
1	3.6 (0.8)	0.38 (0.1)	–	0.6	6.0	2	56
2	3.6 (0.8)	0.38 (0.1)	3.1	2.9	10.0	16	72
3	3.6 (0.8)	0.38 (0.1)	3.7	4.6	11.0	12	80
4	3.6 (0.8)	0.38 (0.1)	6.1	7.4	15.0	18	82
5	3.6 (0.8)	0.38 (0.1)	9.2	8.0	15.0	10	45
6	2.7 (0.6)	0.38 (0.1)	6.1	0.9	15.0	5	73
7	1.8 (0.4)	0.38 (0.1)	6.1	5.5	14.0	5	48
8	0.9 (0.2)	0.38 (0.1)	6.1	8.0	10.0	5	35
9[b]	3.6 (0.8)	0.38 (0.1)	3.7	3.6	12.0	2	98
10[c]	3.6 (0.8)	0.38 (0.1)	3.7	2.0	11.0	4	84
11[d]	3.6 (0.8)	0.38 (0.1)	3.7	3.4	12.4	14	72
12[e]	3.6 (0.8)	0.38 (0.1)	3.7	3.2	9.8	8	66
13[f]	3.6 (0.8)	0.38 (0.1)	3.7	–	–	3	26

[a] Zn$_3$P$_2$ 0.38 mmol; 8 ml of butanol; 2 ml of toluene; 70°C; P(O$_2$) 1 atm; reaction time 6 h; [b] at 60°C; [c] at 50°C; [d] at P(O$_2$) 0.5 atm; [e] at P(O$_2$) 0.2 atm; [f] experiment was carried out under the inert atmosphere.

Table 2. Effect of concentration of CuCl$_2$ catalyst, of reagents and temperature on the rate of oxidation of Zn$_3$P$_2$ and yield of the products in butanol[a]

Exp. no.	x(CuCl$_2$), mmol (g)	x(Zn$_3$P$_2$), mmol (g)	x(HCl), mmol	w(O$_2$)×10^3, M min^{-1}	Q(O$_2$)×10^2, M	Yield, %	
						I	II
1	3.6 (0.48)	0.38 (0.1)	–	2.6	13.4	27	19
2	3.6 (0.48)	0.38 (0.1)	0.57	5.8	13.5	31	29
3	3.6 (0.48)	0.38 (0.1)	1.85	8.4	15.0	42	45
4	3.6 (0.48)	0.38 (0.1)	3.7	8.7	15.2	14	46
5	3.6 (0.48)	0.38 (0.1)	4.6	9.0	15.3	37	42
6	3.6 (0.48)	0.38 (0.1)	5.5	9.6	16.0	34	48
7	3.6 (0.48)	0.38 (0.1)	10. 3	13.0	17.7	18	60
8	0.9 (0.12)	0.38 (0.1)	4.6	2.4	15.7	23	50
9	1.8 (0.24)	0.38 (0.1)	4.6	5.3	15.5	19	57
10	4.5 (0.6)	0.38 (0.1)	4.6	9.6	15.9	27	63
11[b]	3.6 (0.48)	0.38 (0.1)	4.6	6.0	14.8	20	44
12[c]	3.6 (0.48)	0.38 (0.1)	4.6	3.4	13.0	21	34
13[d]	3.6 (0.48)	0.38 (0.1)	4.6	–	–	9	36

[a] Zn$_3$P$_2$ 0.38 mmol; 8 ml of butanol; 2 ml of toluene; 70°C; P(O$_2$) 1 atm; reaction time 6 h; [b] at 60°C; [c] at 50°C; [d] experiment was carried out under the inert atmosphere.

decelerates the O$_2$ absorption, reduces the redox potential value and the total yield of organophosphorus compounds (exps. 5, 11, 12). In the atmosphere of oxygen two parts are observed on potentiometric curves. At the introduction of zinc phosphide redox potential of reaction solution sharply decreases to the cathode area, and then gradually moves to the anode one. At the end of experiments the absorption of oxygen ends, the initial color of solution is restored, and the value of the redox potential approaches the starting one. It shows that Cu(II)/Cu(I) is the potential-forming pair.

In the absence of oxygen the introduction of zinc phosphide in the reaction medium is accompanied by the shift of potential to the cathode area in the course of all experiment, the formation of white precipitate, and discoloration of the solution. This shows that the reduction of Cu(II) ions with phosphide and precipitation of Cu(I) takes place in the system (Fig. 2).

X-ray phase analysis of precipitate showed the presence of phosphorus(V) on its surface together with Cu$^+$ ions in a form of CuCl and Cu$_2$O. It is shown that in the absence of oxygen the oxidative alcoholysis of
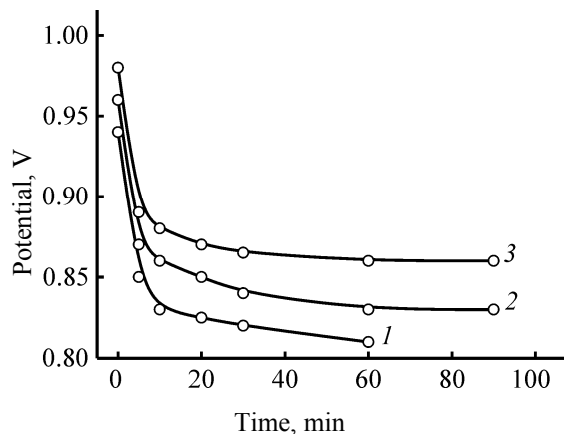
Fig. 2. Potentiometric curves of oxidation of Zn_3P_2 with butanol solution of $CuCl_2$ under the inert atmosphere. $V(BuOH)$ 10 ml; $X(Zn_3P_2)$ 0.38 mmol, $X(CuCl_2)$ 3.6 mmol; T (°C): (*1*) 40, (*2*) 50, and (*3*) 70.

zinc phosphide takes place in $CuCl_2$ butanol solution to give 9% of phosphite **I** and 36% of phosphate **II** (exp. 13).

The chromatographic monitoring of the oxidation of zinc phosphide in the aerobic and anaerobic medium was carried out in $CuBr_2$ butanol solution at 70°C in the course of 5–6 h (Figs. 3a, 3b). The chromatographic analysis of experimental solutions after each hour showed that tributyl phosphate is mainly formed in the reaction mixtures. Its yield constantly grows and in 5 h reaches 80% under oxygen atmosphere and 60% under the inert one. Maximum yield of dibutyl hydrogen phosphite was 10–15%.
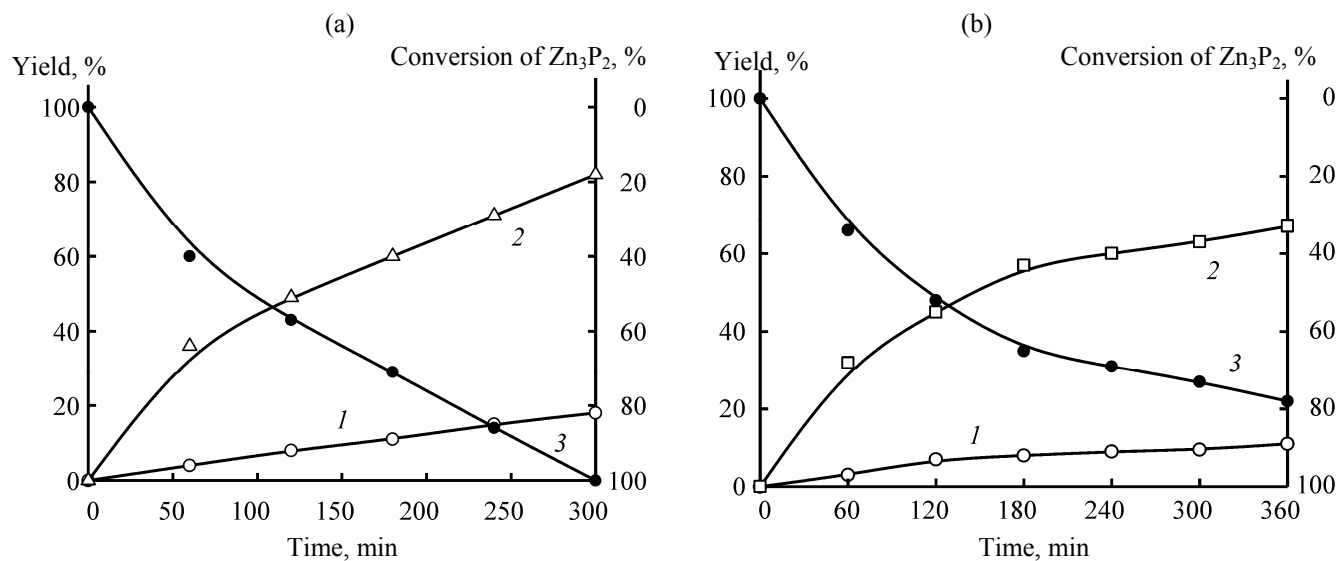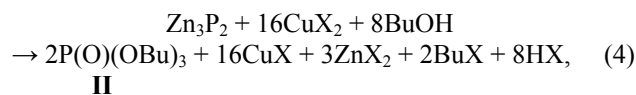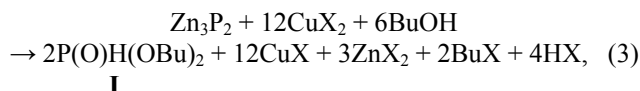
The obtained experimental data permitted to suggest that zinc phosphide and oxygen do not directly react with one another. Catalytic process passes through the following key reactions (3), (4). Zinc phosphide is oxidized with copper(II) halides in butanol to give organophosphorus products.

$$Zn_3P_2 + 12CuX_2 + 6BuOH$$
$$\rightarrow 2P(O)H(OBu)_2 + 12CuX + 3ZnX_2 + 2BuX + 4HX, \quad (3)$$
$$\mathbf{I}$$

$$Zn_3P_2 + 16CuX_2 + 8BuOH$$
$$\rightarrow 2P(O)(OBu)_3 + 16CuX + 3ZnX_2 + 2BuX + 8HX, \quad (4)$$
$$\mathbf{II}$$

$$X = Cl, Br.$$

Oxygen regenerates the catalyst, Cu(I) is oxidized to Cu(II) and returns to the catalytic cycle.

$$4CuX + O_2 + 4HX \rightarrow 4CuX_2 + 2H_2O. \quad (5)$$

The character of variation of redox potential of experimental solutions under oxygen atmosphere confirms the assumed mechanism and shows that in the first part of the potentiometric curve the reduction of Cu(II) to Cu(I) with zinc phosphide takes place with the formation of organophosphorus product [Eqs. (3), (4)], and in the second part the oxidation of the reduced form of catalyst with oxygen [Eq. (5)] occurs.

As a result of performed experiments the promoting action of hydrogen chloride additive on the rate of oxidation of zinc phosphide with oxygen in butanol solutions of copper salts and on the yield of the products was established. Optimal conditions of the process were found to be as follows: 50–70°C, oxygen

Fig. 3. Kinetics of accumulation of organophosphorus compounds in (a) aerobic and (b) anaerobic media. (*1*) $P(O)H(OBu)_2$, (*2*) $P(O)(OBu)_3$, and (*3*) conversion of Zn_3P_2.

pressure 1 at, the molar ratio $CuX_2/Zn_3P_2 = 7–10$, $HCl/Zn_3P_2 = 7–14$. Copper bromide exhibits higher catalytic activity and favors the formation of phosphoric acid ester. In the presence of copper chloride dibutyl hydrogen phosphite and tributyl phosphate are formed. The products were isolated from reaction mixtures by vacuum distillation at the residual pressure 1–10 mm Hg and were identified. In ^{31}P NMR spectra the trialkyl phosphate is characterized by a signal with the chemical shift 0 ± 2 ppm, and dialkyl hydrogen phosphite, by a signal at -8 ± 2 ppm [9]. IR spectra of obtained $P(O)(OBu)_3$ contain typical absorption bands of P=O (1260–1285 cm^{-1}) and P–O–C (1020–1045 cm^{-1}) groups. In the IR spectra of $P(O)H(OBu)_2$ the absorption band at 2430 cm^{-1} belongs to P–H bond vibrations and a band of significantly smaller intensity at 1260 cm^{-1}, to the vibrations of phosphoryl group P=O [10]. Absorption bands of the bending vibrations of methylene groups at 1370–1470 cm^{-1} are also present.

Hence, by the use of catalysts it is possible to obtain organic phosphates and phosphites directly from low-valent phosphorus compounds under mild conditions. Harmless oxidation with oxygen can be used instead of oxidation with toxic chlorine. Catalytic approach developed by us may be also used for performing direct reactions of transition metal phosphides not only with alcohols, but also with the other organic substrates.

EXPERIMENTAL

Environmentally safe oxygen was used as an oxidant. It is often used in organic and inorganic reactions with the participation of copper compounds as catalysts [11].

^1H and ^{31}P NMR spectra were taken on a Bruker Avance II 300 NMR spectrometer. IR spectra were obtained on a Shimadzu IR prestige 21 Fourier IR spectrometer.

Purity of starting zinc phosphide was evaluated by the emission spectral analysis on a DFS-13 device. It was found that the content of impurities was no more than 1%. Granulometric composition and surface of zinc phosphide was evaluated by a Coulter register (TAII model). Particles with the diameter 13.7 μcm prevailed in zinc phosphide sample, and its specific surface was 962 cm^2 g^{-1}. Preliminary drying of butanol was carried out by boiling over CaO and subsequent distillation. Oxygen-argon mixture was dried by passing through calcium chloride.

Oxidative alcoholysis of zinc phosphide was carried out in a closed system on an isothermal installation consisting of the intensely shaken reactor and the burette filled with oxygen. In the course of the experiment Cu(II)/Cu(I) ratio was measured. For this purpose the reactor was equipped with potentiometric device consisting of platinum and calomel electrodes with a joint playing the role of electrolytic key. Experiments were carried out as follows. The reactor was filled with butanol, then a catalyst was placed in it, and the system was flushed with oxygen. After that a weighed sample of zinc phosphide was introduced. The total amount of solution in the reactor was 10–15 ml. The amount of absorbed oxygen, the absorption rate, and the current potential of reaction solution were measured. The quantitative analysis of organophosphorus products against the standard samples was carried out on a Kristall 2000 M chromatograph equipped with a flame ionization detector and a CP SIL 19CB 25 m×0.25 mm capillary column after removing copper salts from the sample by treating with sodium bicarbonate. The conversion of phosphide was calculated on the basis of the yield of organophosphorus compounds. After the reduction of Cu(II) to Cu(I) with thiosulfate and precipitating it with iodide ion dibutyl hydrogen phosphite and tributyl phosphate synthesized were isolated from reaction mixture by vacuum distillation at 5–10 mm and identified by IR and ^{31}P NMR spectroscopy.

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