

CHEMICAL KINETICS
AND CATALYSIS

The Kinetics of Oxidative Alcoholysis of Zinc Phosphide
in the Presence of Oxygen and the FeCl₃–I₂ Mixed Catalyst
in Solution in Butanol

Zh. U. Ibraimova, G. S. Polimbetova, M. M. Aleshkova, and A. K. Borangazieva

*Sokol'skii Institute of Organic Catalysis and Electrochemistry,
Ministry of Education and Science of Kazakhstan, Almaty, Kazakhstan*

e-mail: orgcat@nursat.kz

Received March 17, 2008

Abstract—The oxidative alkoxylation of zinc phosphide to tributyl phosphate occurred at a high rate and with high selectivity in a solution of FeCl₃–I₂ in butanol at 50–70°C. The kinetic characteristics and optimum conditions of the process were determined. The experimental and literature data were used to identify key stages of the formation of tributyl phosphate in the presence of the mixed catalytic system.

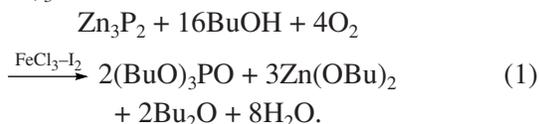
DOI: 10.1134/S0036024409050094

INTRODUCTION

In [1, 2], the oxidative alkoxylation of zinc phosphide (Zn₃P₂) to phosphorus acid esters was studied in the presence of metal complex catalysts on the basis of Cu(II) and Fe(III). The reaction occurred at 60–80°C and followed the separated redox mechanism via the stages of phosphide oxidation by copper or iron chlorides with the formation of an organophosphorus product and catalyst regeneration by oxygen. In the presence of copper(II) as a stronger two-electron oxidizer ($\varphi(\text{Cu(II)} \rightarrow \text{Cu(0)}) = 0.337 \text{ V}$), the reaction yielded pentavalent phosphorus esters, trialkyl phosphates. In a solution of iron(III) chloride in butanol, which more readily participates in one-electron transfer ($\varphi(\text{Fe(III)} \rightarrow \text{Fe(II)}) = 0.771 \text{ V}$), Zn₃P₂ was oxidized by oxygen with the formation of trivalent phosphorus ester, dibutyl phosphite (BuO)₂HPO.

Molecular iodine is well soluble in alcohols and is a fairly strong two-electron oxidizer ($\varphi(\text{I}_2 \rightarrow 2\text{I}^-) = 0.536 \text{ V}$). In the presence of acceptors of iodide ions, iodine easily oxidizes elemental phosphorus to phosphoric acid esters. Electric current, nitrite ions, or transition metal complexes capable of regenerating molecular iodine are used as iodide ion acceptors [3–5].

We found that, at 50–70°C, the addition of a small amount of iodine (~10⁻² mol/l) to a solution of FeCl₃ in butanol contributed to the formation of a more active catalytic system. The rate of the oxidative alkoxylation of Zn₃P₂ increased severalfold in the presence of this system, and the main product formed was tributyl phosphate (BuO)₃PO,



The purpose of this work was to study the kinetic characteristics and determine the optimum conditions and key stages of the oxidation of Zn₃P₂ by oxygen in a solution of FeCl₃–I₂ in butanol.

EXPERIMENTAL

The oxidation of Zn₃P₂ in a catalytic solution was studied in a closed isothermal unit consisting of a reactor, which was intensely shaken, equipped with a potentiometric device and connected to gasometric burettes filled with oxygen. The procedure for measurements was described in detail in [1]. To study the kinetics of the accumulation of organophosphorus compounds (OPCs) during experiments, solution samples were taken in certain time intervals (10–90 min) and subjected to chromatographing. Quantitative analysis of phosphorous and phosphoric acid esters was performed on a Chromopack 9002 chromatograph with a flame ionization detector and a CIPSIL 19 CB capillary column (25000 × 0.25 mm).

The temperature, reagent concentrations, and ratio between mixed catalyst components were varied to determine the kinetics and mechanism of the reaction and select optimum conditions of the formation of tributyl phosphate. The experimental data are presented in the table and Figs. 1–4, where W – Q are the conversion and φ – Q potentiometric curves; W is the rate of oxygen absorption, mol/(l min); Q is the amount of absorbed oxygen, mol/l; φ is the redox potential of the system recalculated to the hydrogen scale, V; and c is the concentration of the OPCs formed.

Oxidative alcoholysis of Zn_3P_2 in the presence of $FeCl_3-I_2$

I_2 , mol/l	$FeCl_3$, mol/l	$W_{max} \times 10^3$, mol/(l min)	c_1 , %	c_2 , %
0	0.5	2.0 (70°C)	53.0	4.0
0	0.3	1.8	13.0	–
0.02	0.2	9.9	22.0	60.0
0.05	0.2	20.0	17.0	67.0
0.1	0.2	19.8	25.0	75.0
0.3	0.2	20.0	8.0	80.0
0.02	0.1	7.5	31.0	29.0
0.02	0.5	12.5	36.0	37.0
0.2	0.3	5.3 ^a	26.0	56.0
0.2	0.3	20.0	10.0	90.0
0.2	0.3	30.0 ^b	13.0	87.0
0.02	0.2	7.2 ^c	21.0	18.0
0.02	0.2	8.1 ^d	33.0	39.0
0.02	0.3	5.3 (50°C)	25.0	54.0
0.02	0.3	10.2	20.0	60.0
0.02	0.3	10.9 (70°C)	27.0	58.0

Note: Reaction conditions 60°C; $p(O_2)$, 10^5 Pa; $[Zn_3P_2] \times 10^2$: 3.9; ^a1.85; and ^b7.8 mol/l; $[BuOH]$: 10.9; ^c2.2; and ^d8.2 mol/l; c_1 and c_2 are the concentrations of $(BuO)_2HPO$ and $(BuO)_3PO$, respectively.

RESULTS AND DISCUSSION

The introduction of Zn_3P_2 into a dark brown $FeCl_3-I_2-BuOH$ solution in the atmosphere of oxygen is accompanied by a sharp shift of the redox potential toward the cathode region by 0.1–0.2 V, solution clarification, and the beginning of oxygen absorption. The absorption of oxygen restores the initial color of the catalytic solution and shifts the potential toward its initial value. The rate of the reaction is low at its beginning but rapidly increases to a maximum value and then decreases to zero (Figs. 1, 2). The conversion and potential change in parallel, and the amount of absorbed O_2 corresponds to the stoichiometry of reaction (1). The reaction solution contains two potential forming pairs, $I_2/2I^-$ and Fe^{3+}/Fe^{2+} , but the equilibrium potential of iodine is attained faster, and it determines the redox potential of the system. This follows from the shape of the potentiometric curves and cyclic color changes.

Figure 1 shows that a change in the concentration of iodine at 60°C in a solution of $FeCl_3$ in butanol from 0 to 0.05 mol/l contributes to an increase in the initial potential of the system, cathode and anode shift, and an increase in the rate of the reaction by ~10 times. In the absence of iodine, an alcoholic solution of $FeCl_3$ at 70°C absorbs oxygen at a low rate, the main reaction product is dibutyl phosphite (53%), and only 4% tributyl phosphate is formed. In a mixed catalytic system,

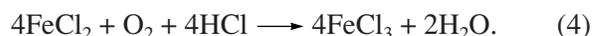
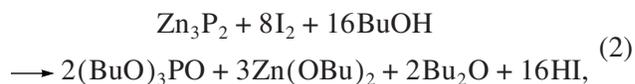
zinc phosphide is oxidized by oxygen with the predominant formation of tributyl phosphate, whose yield increases as the concentration of iodine grows and, at a 0.3 mol/l concentration, is 80%. The yield of dibutyl phosphite is then 8% (table). In the absence of iron, an 0.02 mol/l solution of iodine in alcohol does not absorb oxygen, and organophosphorus products are not formed. An increase in the concentration of iron to 0.5 mol/l increases the rate of the reaction, but the yield of tributyl phosphate is maximum (60%) at a $FeCl_3/I_2$ ratio of 10. Changes in the temperature over the range 50–70°C increase the rate of oxidation of Zn_3P_2 and insignificantly influence the yield of tributyl phosphate (table, Fig. 2).

The kinetic curves of the accumulation of organophosphorus compounds in the oxidative alcoholysis of zinc phosphide in the presence of oxygen and the $FeCl_3-I_2$ mixed catalyst are shown in Fig. 3. We see that, under the conditions studied, phosphoric and phosphorous acid esters are formed at the very beginning of experiments, and the concentrations of tributyl phosphate and dibutyl phosphite reach 6.0×10^{-2} and 1.8×10^{-2} mol/l, respectively, in 30–45 min. The total yield of butyl esters corresponds to a 100% conversion of zinc phosphide.

The rate of the reaction and the yield of the main product increase as the concentrations of the reagents (Zn_3P_2 , $BuOH$, and O_2) grow. Zinc phosphide is also oxidized under anaerobic conditions with the formation of tributyl phosphate (60%).

The dependences of the yields of tributyl phosphate and dibutyl phosphite and the highest reaction rate on the ratio between the catalyst components are shown in Fig. 4. An analysis of the experimental data shows that the $FeCl_3-I_2$ mixed catalytic system exhibits synergic properties. Pure components show insignificant activity in the oxidative alcoholysis of Zn_3P_2 . The rate of the reaction and the amount of tributyl phosphate formed pass maxima as the $FeCl_3/I_2$ ratio increases from 2 to 50, and the yield of dibutyl phosphite continuously grows. The highest reaction rate is observed at a $FeCl_3/I_2$ ratio of 10, the maximum yield of $(BuO)_3PO$, at a $FeCl_3/I_2$ ratio of 5, and the maximum yield of dibutyl phosphite, at $[I_2] = 0$.

Our and literature data [3–7] suggest the two-stage (separated) redox mechanism for the oxidation of Zn_3P_2 with oxygen in a solution of $FeCl_3-I_2$ in butanol. This mechanism involves the reactions



Molecular iodine is a stronger two-electron oxidizer responsible for the formation of tributyl phosphate (reaction (2)). $FeCl_3$ plays the role of the acceptor of hydrogen iodide produced (3) and returns into the cata-

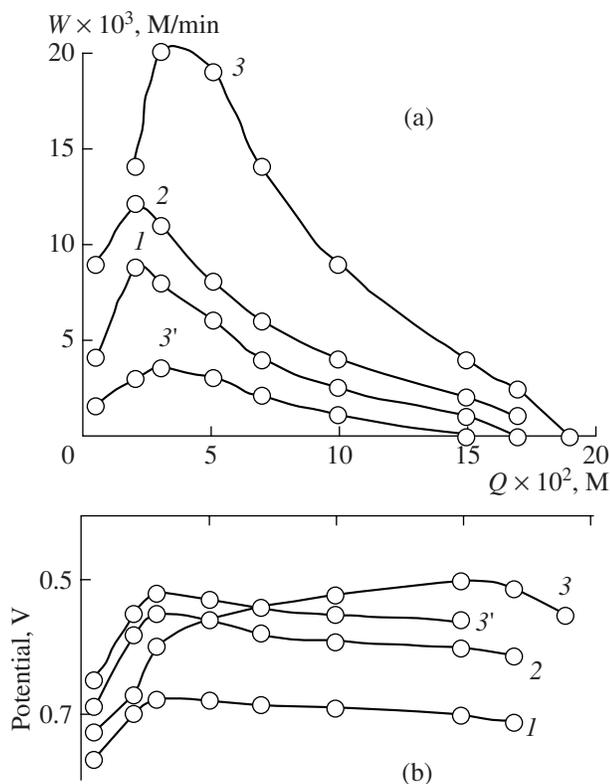


Fig. 1. (a) Conversion and (b) potentiometric curves of the oxidative alcoholysis of Zn_3P_2 in a solution of $FeCl_3-I_2$ in butanol at $60^\circ C$, $p(O_2) = 10^5$ Pa, and reagent concentrations, mol/l: BuOH, 10.9; Zn_3P_2 , 3.9×10^{-2} ; $FeCl_3$, 0.2, I_2 (1) 0.02, (2) 0.03, (3) 0.05; and $FeCl_3$, 0.4; ($3'$) I_2 , 0.0, $70^\circ C$.

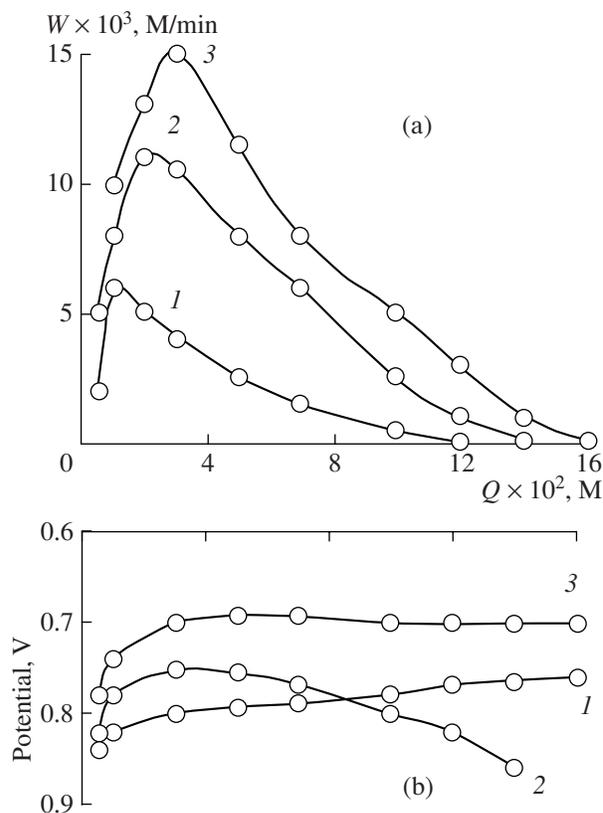


Fig. 2. Oxidative alcoholysis of Zn_3P_2 at $p(O_2) = 10^5$ Pa, reaction solution component concentrations, mol/l: BuOH, 10.9; $FeCl_3$, 0.3; I_2 , 0.02; Zn_3P_2 , 3.9×10^{-2} ; temperature: (1) 50, (2) 60, and (3) $70^\circ C$.

lytic cycle in reaction (4). The catalysis of overall process (1) is performed because of the distribution of functions between the mixed catalyst components.

The suggested mechanism is substantiated by the identity of the products obtained under aerobic and anaerobic conditions and the presence of extrema of conversion and potentiometric curves. The cathode redox potential shift at the beginning of experiments is evidence that the ascending portion of the conversion curve is related to the predominant occurrence of reaction (2) (Figs. 1, 2). Along the descending portion, the predominant processes are the regeneration of the catalytic system components accompanied by the gradual return of the potential to its initial value and cessation of oxygen absorption. At the maximum point, the rates of I_2 reduction and regeneration are close to each other.

The experimental data and the suggested separated redox mechanism were used to derive the equation describing the kinetic characteristics of process (1) in the presence of $FeCl_3-I_2$,

$$W_{\max} = \frac{k_{\text{red}}[Zn_3P_2][BuOH][I_2]k_{\text{ox}}[FeCl_3][O_2]}{k_{\text{ox}}[FeCl_3][O_2] + k_{\text{red}}[Zn_3P_2][BuOH]}, \quad (5)$$

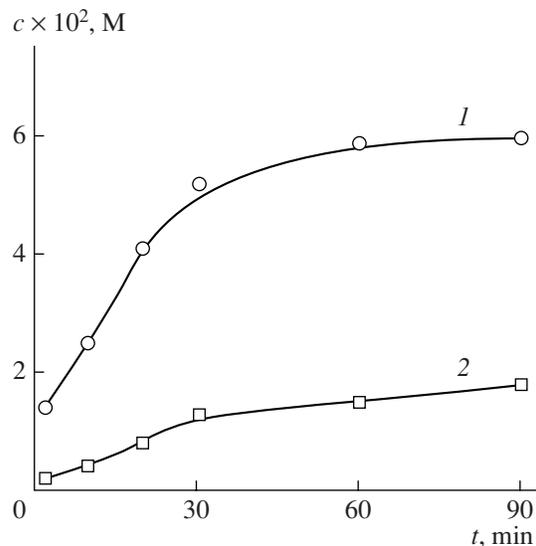


Fig. 3. Kinetic curves of the accumulation of (1) tributyl phosphate and (2) dibutyl phosphite in the oxidative alcoholysis of Zn_3P_2 in butanol at $60^\circ C$, $p(O_2) = 10^5$ Pa, $[FeCl_3] = 0.2$, $[Zn_3P_2] = 3.9 \times 10^{-2}$, and $[I_2] = 0.04$ mol/l.

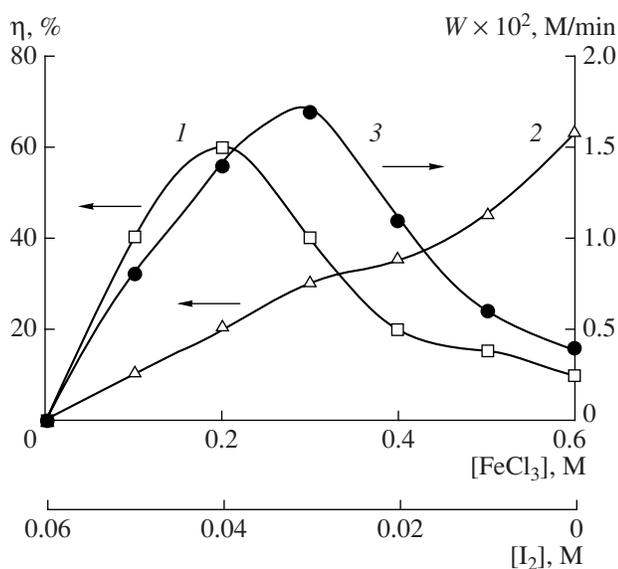


Fig. 4. Dependences of the yield (η , %) of (1) tributyl phosphate and (2) dibutyl phosphite and (3) the rate of oxidative alcoholysis of Zn_3P_2 in butanol on the ratio between the FeCl_3 - I_2 mixed catalyst components at 60°C , $p(\text{O}_2) = 10^5$ Pa, and $[\text{Zn}_3\text{P}_2] = 3.9 \times 10^{-2}$ mol/l.

where k_{red} is the rate constant for the reduction of I_2 with phosphide, $\text{l}^2/(\text{mol}^2 \text{ min})$; k_{ox} is the rate constant for the oxidation of $\text{Fe}(\text{II})$ with oxygen, $\text{l}/(\text{mol min})$; $[\text{Zn}_3\text{P}_2]$, $[\text{BuOH}]$, $[\text{FeCl}_3]$, $[\text{O}_2]$, and $[\text{I}_2]$ are the reagent concentrations in solution; and W_{max} is the maximum rate of oxygen absorption. The equation was derived using the assumptions suggested in [4].

The k_{red} and k_{ox} values ($6.0 \times 10^{-2} \text{l}^2/(\text{mol}^2 \text{ min})$ and $8.5 \text{l}/(\text{mol min})$ at 60°C , respectively) were calculated by graphically solving Eq. (5). The activation energy and entropy of reaction (2) found from the temperature

dependence were 43.0 kJ/mol and $-103.0 \text{ J}/(\text{mol K})$, respectively. The calculated kinetic and activation parameters are indicative of a higher catalytic activity of the mixed system compared with the individual FeCl_3 catalyst [2]. The driving forces of the oxidative P-O coupling between Zn_3P_2 and alcohols are the high energies of the P-O and P=O bonds formed (335 and 544 kJ/mol) and the redox potential of the $\text{I}_2/2\text{I}^-$ pair.

To summarize, the oxidative alkoxylation of Zn_3P_2 with the selective formation of trialkyl phosphate under mild conditions can be performed using a new effective catalytic system including iron trichloride and iodine. Because of the separation of functions between the mixed catalyst components, the reaction follows a route more favorable thermodynamically.

REFERENCES

1. Ya. A. Dorfman, Zh. U. Ibraimova, and G. S. Polimbetova, *Zh. Fiz. Khim.* **76** (1), 61 (2002) [*Russ. J. Phys. Chem.* **76** (1), 50 (2002)].
2. Zh. U. Ibraimova, G. S. Polimbetova, M. M. Aleshkova, and A. K. Borangazieva, *Zh. Fiz. Khim.* **78** (8), 1443 (2004) [*Russ. J. Phys. Chem.* **78** (8), 1265 (2004)].
3. V. V. Turygin, Extended Abstract of Candidate's Dissertation in Technical Science (Moscow, 1999).
4. Ya. A. Dorfman, R. R. Abdreimova, G. S. Polimbetova, et al., *Kinet. Katal.* **37** (2), 199 (1996) [*Kinet. Catal.* **37** (2), 183 (1996)].
5. M. M. Aleshkova, G. O. Bugubaeva, and G. S. Polimbetova, *Zh. Obshch. Khim.* **75** (8), 1259 (2005) [*Russ. J. Gen. Chem.* **75** (8), 1193 (2005)].
6. N. G. Feshchenko and Zh. K. Gorbatenko, *Zh. Obshch. Khim.* **62** (7), 1481 (1992).
7. N. G. Feshchenko, A. V. Kirsanov, V. G. Kostina, et al., in *Chemistry and Application of Organophosphorous Compounds* (Nauka, Leningrad, 1987), p. 342 [in Russian].