

## Oxidation of Sodium Hypophosphite by Oxygen in Alcoholic Solutions of Ferrum (III)

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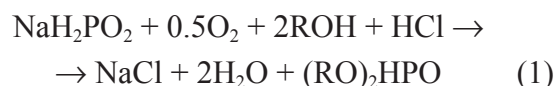
### Abstract

Hypophosphites are widely used as reducers in the metal protection coating, as reagents in the synthesis of various organophosphorus compounds, in analytical chemistry, and in many other fields.  $\text{NaH}_2\text{PO}_2$  difficultly reacts with many oxidizers without catalysts despite of the significant reduction potential. The kinetics and the mechanism of hypophosphite oxidation in aqueous acid solution of the metal and nonmetal salts are studied in detail. The reactivity of hypophosphite in the organic solvents was not almost studied. In this work the basic possibility of synthesis dialkylphosphites from cheap, accessible and harmless  $\text{NaH}_2\text{PO}_2$  and alcohols is shown. Sodium hypophosphite is oxidized by oxygen in alcoholic solutions of  $\text{FeCl}_3$  at 50–80°C to dialkylphosphites. Kinetic and mechanism of the reaction are investigated by methods of volumetry, redox-potentiometry, GC, IR-, UV-, EPR-, Mössbauer- and NMR  $^{31}\text{P}$ -spectroscopy and X-ray powder diffraction analysis, optimum conditions are found, kinetic and activation parameters of the reaction are calculated. It is shown, that the process follows redox-mechanism and consists of two key stages: reduction of Fe (III) by hypophosphite with formation of dialkylphosphite and reoxidation of Fe (II) by oxygen. The coordination mechanism of reduction reaction of Fe (III) by hypophosphite is proposed. According to this mechanism the dialkylphosphite forms through innersphere redox-decomposition of intermediate alcoxyhypophosphite complex of Fe (III). The coordination mechanism of the process is confirmed by low values of  $E^\ddagger$  and negative activation entropies  $\Delta S^\ddagger$ . The availability in an inner sphere of Fe (III) bromide, low-molecular alcohols, water, characterized by high acidity, increases the reaction rate of oxidative alcoxilation of hypophosphite and promotes the further transformation of dialkylphosphite to di- and trialkylphosphate.

### Introduction

The existent technology of phosphoric ether production is based on multistep processes of toxic, flammable and explosive white phosphorus oxidation by chlorine up to  $\text{PCl}_3$ ,  $\text{POCl}_3$  followed by the alcoxilation and is accompanied by formation of a considerable quantity of toxic hydrogen chloride. In this connection the development direct catalytic oxidation of low-valence inorganic phosphorus compounds by oxygen to phosphoric ethers is an actual problem [1]. Cheap, accessible and harmless sodium hypophosphite is one of the most perspective phosphorylation agents.  $\text{NaH}_2\text{PO}_2$  difficultly reacts with many oxidizers without presence of catalysts despite of the significant reduction potential [2-5].

In the present work kinetics and mechanism of sodium hypophosphite oxidation by oxygen in alcoholic solutions ( $\text{ROH} = \text{PrOH}$ ,  $\text{BuOH}$ , *i*- $\text{AmOH}$ ) of iron (III) chloride are studied for the first time. It is established, that dialkylphosphites are formed at 50–80°C via reaction (1)



Due to high reactivity dialkylphosphites are widely used in organic synthesis to deriving medicines and bioactive substances.

### Experimental

Reaction (1) was investigated by volumetric method of oxygen absorption using the thermostatted catalytic reactor in the form of a long-necked flask

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with a potentiometric device and a gas burette. The experiments were conducted as follows. An alcohol (10 ml) was poured into the reactor (150 cm<sup>3</sup>) and an iron salt (0.3-1.5 g) as a powder was added. The content was shaken until the redox-potential was constant. Then sodium hypophosphite was added in it and the rate of oxygen absorption ( $W$ , mol/l-min), the amount of the absorbed oxygen ( $Q$ , mol/l), redox-potential ( $\varphi$ , V) and time ( $\tau$ , min) were measured. The experimental data are presented as conversion ( $W$ - $Q$ ), kinetic ( $W$ - $\tau$ ) and potentiometric ( $\varphi$ - $\tau$ ,  $\varphi$ - $Q$ ) curves. The relative error in measuring the O<sub>2</sub> absorption rate was 4-6%. Organic hypophosphites, phosphites, phosphates were identified by the method of NMR <sup>31</sup>P-spectroscopy (WP-80, WM-250 Bruker). Gas chromatography analysis of alcohols, dialkylphosphites ((RO)<sub>2</sub>HPO) and trialkylphosphates ((RO)<sub>3</sub>PO) were recorded on Chrompack 9002 chromatograph using PID with a programmed column heating from 130 to 150°C at rate of gas-carrier (Ar) 25 ml/min and evaporator temperature 360°C on CIPSIL 19CB capillary column (25 m × 0.25 mm). Dialkylphosphates were isolated by vacuum distillation in the form of the resin and were identified by the method of IR-spectroscopy on the spectrometer Specord IR-75 by the typical absorption bands of groups P(O)OH (2600 cm<sup>-1</sup>), P=O (1220 cm<sup>-1</sup>) and P-O-C (1040 cm<sup>-1</sup>). Alkoxyhypophosphite complexes of Fe (III) were investigated by the method of UV-spectroscopy (Spectrometer SF-46). The EPR spectra of Fe (III) alcoholic solutions were recorded on a YES-Me-3X spectrometer. The Mössbauer-spectra were taken on SM 2201 relatively  $\alpha$ -Fe and NSP. The X-ray powder diffraction analysis of precipitates formed was carried out on Dron-4 instrument.

## Results and Discussion

The influence of the component concentrations and the temperature of catalytic system on the process rate and selectivity were investigated with the purpose of establishing kinetics, mechanism and optimum conditions of reaction (1). The typical conversion, kinetic and potentiometric curves of oxidation NaH<sub>2</sub>PO<sub>2</sub> by oxygen (10<sup>5</sup> Pa) in butanol solution of FeCl<sub>3</sub> at 80°C are shown in Figs. 1-3. Addition NaH<sub>2</sub>PO<sub>2</sub> into the dark yellow alcoholic solution of Fe (III) in the O<sub>2</sub> atmosphere results in a shifting of system's redox-potential to the cathode region on 0.05-0.2 V, depending on the solution composition. Also it is observed the simultaneous decrease of pressure in the closed

system accompanied by oxygen absorption, brightening of the solution, and presipitation of a white solid. The amount of absorbed oxygen is in accordance with reaction (1). During experiment  $\varphi_{\text{Fe(III)}}$  gradually shifts to the anode region, the reaction rate quickly increases, reaches maximum, and then gradually falls up to zero. The solution containing a small amount of the white precipitate acquired its initial colour. The X-ray powder diffraction analysis showed that the main reflections correspond to NaCl.

*Influence of NaH<sub>2</sub>PO<sub>2</sub>* – Increasing concentration of hypophosphite from 0.06 up to 0.36 mol/l increases the reaction rate and the amount of absorbed oxygen. The yield of dialkylphosphite slightly decreases (Fig. 1, Table 1). The reaction order in hypophosphite is equal to 0.7. The formation of alkoxyhypophosphite complexes of Fe (III) is confirmed by UV-spectra of solutions under study (Fig. 1c). In the absence of hypophosphite, the alcoholic solution of FeCl<sub>3</sub> has the absorption band with the maximum at 370 nm (Spectrum 1). With an addition of NaH<sub>2</sub>PO<sub>2</sub> to the system and with the increase in its concentration, the displacement of wavelength maximum in short-wave area up to 260 nm and increase of its intensity is observed. The constant of stability defined from spectrophotometric data makes magnitude 2.1, from kinetic data – 3.6 l/mol.

*Influence of Fe (III), O<sub>2</sub> concentrations and temperature* – Increasing concentration of Fe (III), partial pressure of oxygen, temperature increases reaction rate, value of initial potential and yield of the product (Table 1). The amount of absorbed oxygen remains constant and corresponds to the stoichiometry of the reaction (1). The orders on Fe (III) and O<sub>2</sub> are close to 1. The kinetic regularities indicate the participation of mononuclear alkoxyhypophosphite Fe (III) complexes in reaction (1) that also is confirmed by UV- and EPR-spectra.

*Influence of the alcohol* – Decreasing of BuOH concentration up to 1.1 mol/l at constant concentration of remaining components results in a diminution of reaction rate and yield of product (Fig. 2, Table 1). The reaction order in the alcohol concentration is equal 0.8. The UV-spectra of FeCl<sub>3</sub> aqueous-alcoholic solutions testify to formation of Fe (III) alkoxy-complexes (Fig. 2c). With increasing of alcoholic concentration grows the optical density of a solution, the absorption band with the maximum at 290 nm shifts toward long-wave region. The stability constant found from spectrophotometric data is 0.08, while that found from the kinetic data is 0.1 l/mol.

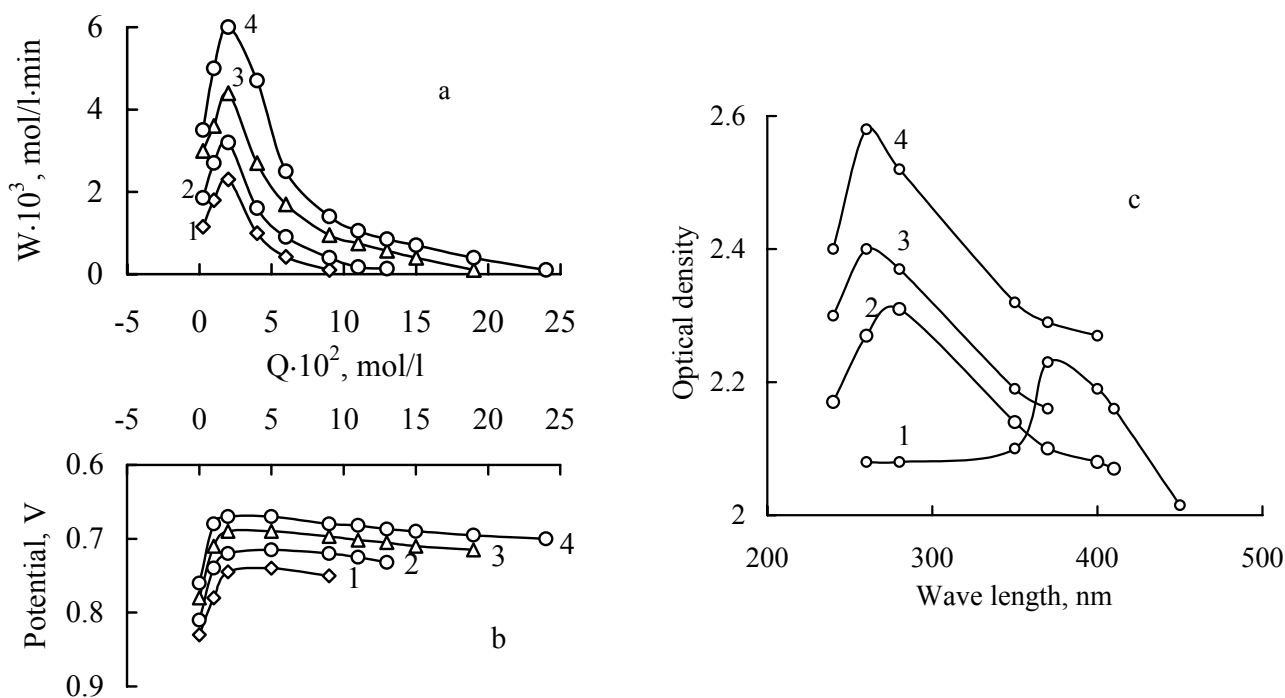


Fig. 1. Conversion (a) and potentiometric (b) curves of  $\text{NaH}_2\text{PO}_2$  oxidation by oxygen in butanol solution of  $\text{FeCl}_3$  at  $80^\circ\text{C}$ ,  $\text{O}_2$   $10^5$  Pa and following concentration of components, mol/l:  $\text{FeCl}_3$  0.6; BuOH 10.9;  $\text{NaH}_2\text{PO}_2$ : 1 – 0.06; 2 – 0.12; 3 – 0.24; 4 – 0.36; c) Absorption spectras of solutions BuOH– $\text{FeCl}_3$ – $\text{NaH}_2\text{PO}_2$  at  $25^\circ\text{C}$ ,  $\text{FeCl}_3$  0.012; BuOH 10.9;  $\text{NaH}_2\text{PO}_2$ : 1 – 0; 2 – 0.023; 3 – 0.046; 4 – 0.069, mol/l.

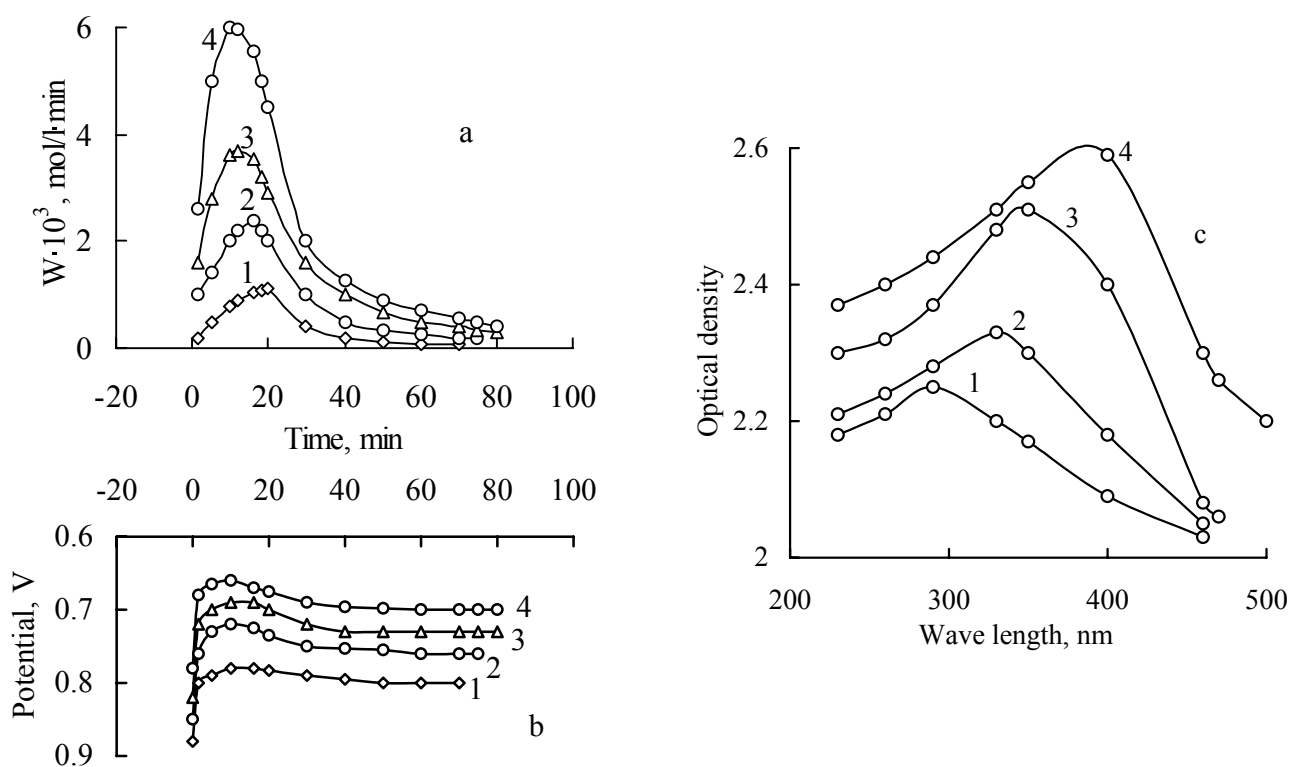


Fig. 2. Kinetic (a) and potentiometric (b) curves of oxidation  $\text{NaH}_2\text{PO}_2$  by oxygen in butanol solution of  $\text{FeCl}_3$  at  $80^\circ\text{C}$ ,  $\text{O}_2$   $10^5$  Pa and following concentration of components, mol/l:  $\text{FeCl}_3$  0.6;  $\text{NaH}_2\text{PO}_2$  0.36; BuOH: 1–1.1; 2–3.3; 3–5.5; 4–10.9; c) Absorption spectras of solutions  $\text{FeCl}_3$ –PrOH– $\text{H}_2\text{O}$  at  $25^\circ\text{C}$ ,  $\text{FeCl}_3$  0.062; PrOH: 1–0; 2–6.5; 3–10.5; 4–13.1, mol/l.



**Table 1**  
Continued

Composition of the solution, mol/l			T, °C	O <sub>2</sub> , vol.%	Yield (η), %	
FeCl <sub>3</sub>	NaH <sub>2</sub> PO <sub>2</sub>	ROH			(RO) <sub>2</sub> HPO	(RO) <sub>3</sub> PO
		PrOH				
0.6	0.36	13.4	50	100	3.0	15.0
			60		6.0	24.0
			70		10.0	43.0
			80		10.0	41.0

<sup>a</sup>dioxan is used as solvent

*Influence of the acid* – In interval of HCl concentration from 0 up to 0.7 mol/l the rate of reaction (1) increases, the yield of the dialkylphosphite slightly decreases (Fig. 3, Table 1). The reaction order on HCl is equal 0.8. The UV-spectrum of FeCl<sub>3</sub>–BuOH solution contains absorption band with a maximum at 370 nm that corresponds to the molecular form of FeCl<sub>3</sub> (Fig. 3c, Spectrum 1). In the presence of HCl the spectrum exhibits the absorption bands due to the anionic form FeCl<sub>4</sub><sup>-</sup> (Spectra 2, 3), which is most

active in reaction (1). With increasing of HCl concentration the intensity of this band increases. Obtained results are in agreement with authors' works [6-8]. The stability constant of tetrachloroferrate complex FeCl<sub>4</sub><sup>-</sup>, calculated from the spectrophotometric data, is 0.7, while the calculations from the kinetic data give the value of 0.5 l/mol.

Under optimal conditions, the yield of dialkylphosphites is 70-80%, di-, trialkylphosphates – 20-30%. The molar ratio of final products depends on

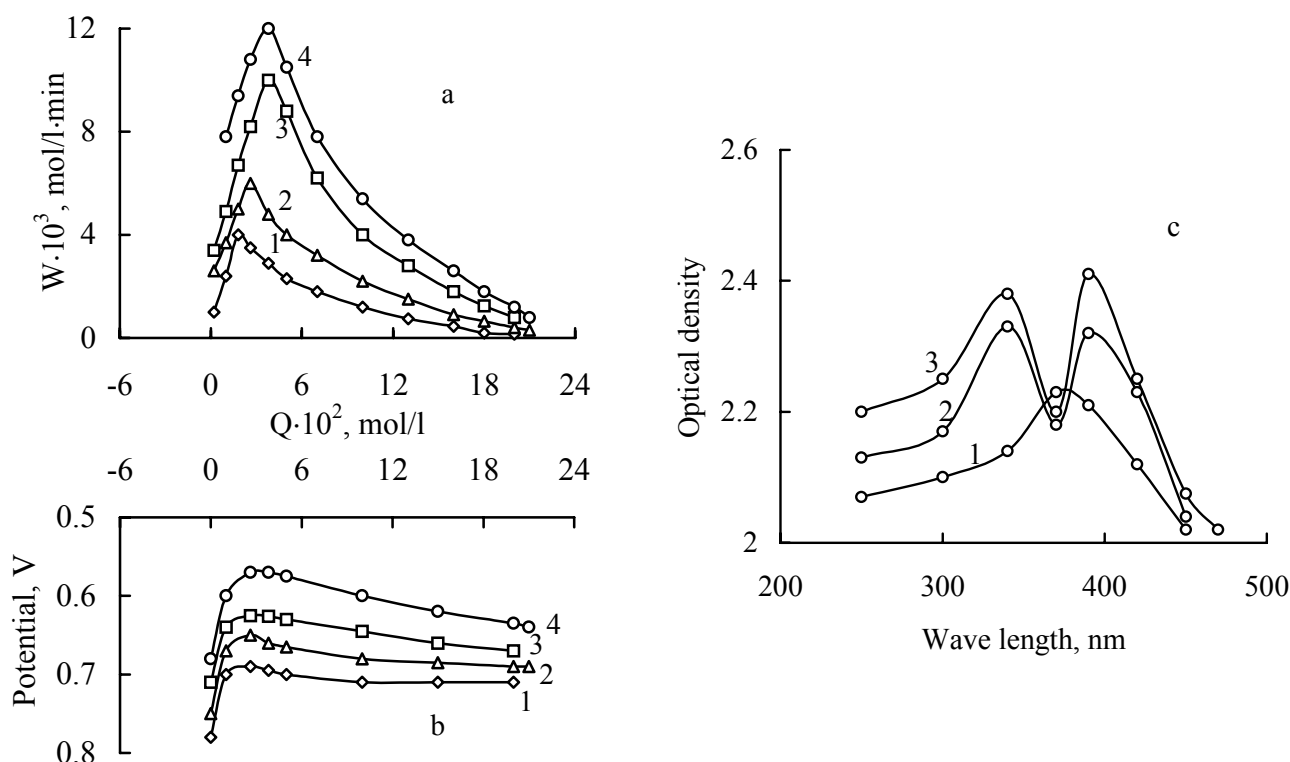
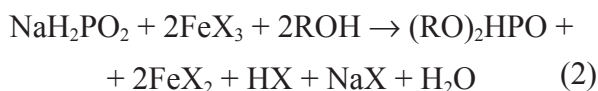


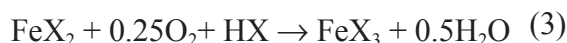
Fig. 3. Conversion (a) and potentiometric (b) curves of oxidation NaH<sub>2</sub>PO<sub>2</sub> by oxygen in butanol solution of FeCl<sub>3</sub> at presence of HCl at 70°C, O<sub>2</sub> 10<sup>5</sup> Pa and following concentration of components, mol/l: FeCl<sub>3</sub> 0.6; BuOH 10.9; NaH<sub>2</sub>PO<sub>2</sub> 0.36; HCl: 1 – 0; 2 – 0.3; 3 – 0.5; 4 – 0.7; 5 – 1.0; c) Absorption spectras of solutions FeCl<sub>3</sub>–BuOH–HCl at 25°C, FeCl<sub>3</sub> 0.12; HCl: 1 – 0; 2 – 0.25; 3 – 1.5, mol/l.

nature of alcohols and Fe (III) salts. The yield of dialkylphosphites is reduced by transition to low molecular alcohols (PrOH), and by replacement FeCl<sub>3</sub> on FeBr<sub>3</sub> (Table 1).

In argon atmosphere Fe (III) is reduced by hypophosphite up to Fe (II) with formation of dialkylphosphite (Table 1).



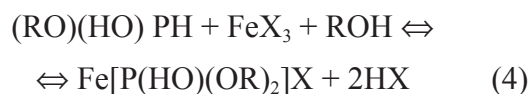
Introduction of O<sub>2</sub> in this system results to reoxidation of FeX<sub>2</sub>



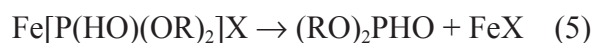
The Mössbauer spectra of "in situ" solutions showed, that the content of Fe (III) in Ar atmosphere gradually decreased up to 22%, and the amount of Fe (II) reached 88%. Noticeable diminution of quadrupole splitting ( $\Delta$ ) and downward tendency of isomeric shift ( $\delta$ ) were observed for trivalent state during experiment that testifies to coordination of acceptor ligands. In oxygen atmosphere the content of Fe (II) in a point corresponding to the maximum rate reached 15% and decreased up to 13.5% in the end of experiment. However, the gradual diminution of quadrupole splitting for trivalent state testified that the reduction proceeds constantly. The Fe (III) parameters changed as compared to the initial state, thus pointing to the ligand coordination and the formation of more symmetric environment of Fe<sup>3+</sup> ion. The Fe (II) forms also changed during the experiment, which suggests the change in its ligand environment

The identity of products obtained in aerobic and anaerobic conditions, the data of Mössbauer spectroscopy, extremal patterns of the conversion, kinetic and potentiometric curves have allowed concluding about the separate redox-mechanism of a reaction (1). The initial section of the curves corresponds to the predominant process of Fe (III) reduction with hypophosphite (2), in the descending section, the Fe (II) reoxidation with oxygen (3) prevails. The rates of both processes are equal at the maximum point. Insofar as the oxidation of Fe (II) with molecular oxygen has been studied quiet thoroughly, our attention was primarily given to the mechanism of reaction (2). The obtained physicochemical regularities, physicochemical data, and the literature data on the reactions of hydrophosphoryl compounds [9,10] and on the redox processes including the Fe (III) complexes allowed us to propose the coordination mechanism of Fe (III) reduction with hypophosphite. Ac-

cording to NMR <sup>31</sup>P spectra sodium hypophosphite in alcoholic solution exists mainly as alkylhypophosphite (RO)H<sub>2</sub>PO, described by a chemical shift 14.91 ppm [11]. At the presence of transitional metal ions alkylhypophosphite fast transforms in hydroxy-derivative RO(HO)PH [12]. Due to availability of unshared pair of electrons the tautomeric form forms metal complexes that are confirmed by the NMR <sup>31</sup>P spectrum of the reaction solution (-11.3 ppm). Like the other bonds of H atoms with heteroatoms, the acidity of the P-H bond sharply increases as the result of coordination, which favors its dissociation and HX elimination from the complexes.



In limiting stage (5) innersphere redox-decomposition of intermediate alcoxyhypophosphite complex of Fe (III) take place with formation of dialkylphosphite and Fe (I), that is quickly oxidized to Fe(II) (6):



No homolytic one-electron decomposition is observed since the use of inhibitor of radicals – quinone, does not hinder process. Oxidizing heterolysis is facilitated at presence of ligands forming complexes with the reduced form [13].

At pH constant the reaction rate at the maximum point is described by the following equation:

$$\begin{aligned} W_{\max} &= k_{\text{red}}[\text{NaH}_2\text{PO}_2][\text{ROH}][\text{FeX}_3] = \\ &= k_{\text{ox}}[\text{FeX}_2][\text{O}_2] \quad (7) \end{aligned}$$

where [NaH<sub>2</sub>PO<sub>2</sub>], [ROH], [FeX<sub>3</sub>], [FeX<sub>2</sub>], [O<sub>2</sub>] – reagent concentrations in a liquid phase,  $k_{\text{red}}$  – constant of rate of Fe (III) reduction, mol<sup>-2</sup>·l<sup>2</sup>·min<sup>-1</sup>,  $k_{\text{ox}}$  – constant of rate of oxidation Fe (II) by oxygen, mol<sup>-1</sup>·l·min<sup>-1</sup>. Concentration of O<sub>2</sub> in a liquid phase is calculated taking into consideration the influences of temperature, partial pressure and effect of salts. Concentration of NaH<sub>2</sub>PO<sub>2</sub> is calculated from the amount of absorbed oxygen at the moment.

The kinetic equation was derived, using method of stationary concentration and balance for the catalyst forms and having in mind that at the maximum point  $W_{\max} = W_{\text{ox}} = W_{\text{red}}$ .

$$W_{\max} = \frac{k_{\text{red}}[\text{NaH}_2\text{PO}_2][\text{ROH}][\text{Fe}]_{\Sigma}k_{\text{ox}}[\text{O}_2]}{k_{\text{ox}}[\text{O}_2] + k_{\text{red}}[\text{NaH}_2\text{PO}_2][\text{ROH}]} \quad (8)$$

where [Fe]<sub>Σ</sub> = [Fe(III)] + [Fe(II)] – total concentra-



tion of iron. For description of reaction (1) the kinetic ( $k_{red}$ ,  $k_{ox}$ ) and activation parameters ( $E_{red}^\ddagger$ ,  $E_{ox}^\ddagger$ ,  $\Delta S_{red}^\ddagger$ ,  $\Delta S_{ox}^\ddagger$ ) were calculated (Table 2) by graphic solution of equation (8). The coordination mechanism of the process is confirmed by low values of  $E^\ddagger$  and the negative activation entropies  $\Delta S^\ddagger$  (Table 2).

The availability in inner sphere of Fe (III) bromide, low-molecular alcohols and molecules of water characterized by high acidity increases a rate of a reaction of oxidative alcoxilation of hypophosphite and promotes the further transformation of dialkylphosphite in di- and trialkylphosphate.

**Table 2**

Kinetic and activation parameters of oxidation reaction of  $\text{NaH}_2\text{PO}_2$  by oxygen in alcohol solution of Fe (III) salts at 70°C

$\text{FeX}_3$	ROH	$k_{red} \cdot 10^3$ , $\text{l}^2/\text{mol}^2 \cdot \text{min}$	$k_{ox}$ , $\text{l}/\text{mol} \cdot \text{min}$	$E_{red}^\ddagger$ , kJ/mol	$E_{ox}^\ddagger$ , kJ/mol	$S_{red}^\ddagger$ , J/mol·K	$S_{ox}^\ddagger$ , J/mol·K
$\text{FeCl}_3$	PrOH	2.0	1.5	39.0	41.0	-196.0	-137.0
$\text{FeCl}_3$	BuOH	1.5	1.1	54.0	56.0	-157.0	-92.0
$\text{FeCl}_3$	<i>i</i> -AmOH	1.2	0.9	63.0	67.0	-133.0	-71.0
$\text{FeBr}_3$	BuOH	1.8	1.4	51.0	54.0	-170.0	-125.0

## Conclusions

Thus, the possibility of dialkylphosphites synthesis from cheap, accessible and harmless  $\text{NaH}_2\text{PO}_2$  and alcohols was shown. The kinetics of the process was studied. The separate redox-mechanism of  $\text{NaH}_2\text{PO}_2$  oxidation by oxygen at the presence of Fe (III) complexes was offered. Kinetic and activation parameters of the new reaction were calculated.

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