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Bifunctional Metal Complex Catalysts for the Processes of Fine Organic Synthesis

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Abstract

Modern approaches to the development of ecologically and economically acceptable methods for obtaining a number of industrially essential products are considered. The promising character of the application of phase-transfer catalysis method for reactions proceeding in liquid two-phase systems with the use of ecologically favourable oxidizing agent – hydrogen peroxide – was demonstrated. Results of integrated studies of the structural characteristics of tungsten peroxopolyoxocomplexes formed in the interaction of the aqueous solutions of phosphotungstic heteropolyacid with hydrogen peroxide by means of EXAFS, Raman and IR spectroscopy are presented. The synthesized catalysts $Q_3\{PO_4[WO(O_2)_2]_4\}$, where Q_3 is a quaternary ammonium cation, were tested in the reactions of oxidation of organic substrates with 30–35 % H_2O_2 solutions.

Key words: peroxopolyoxometallates, EXAFS, Raman and IR spectroscopy, phase-transfer catalysts, fine organic synthesis

INTRODUCTION

Existing production in the area of fine organic synthesis, as a rule, involves multistage processes and is characterized by a large amount of wastes. The values of E factor for separate branches of industry are shown below:

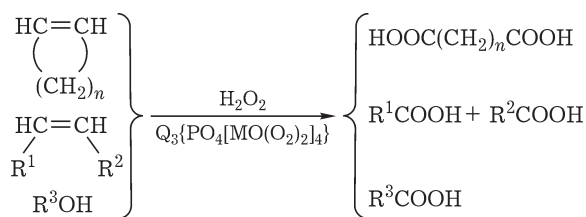
Branches	Tonnage, t/year	E factor, kg of wastes/kg of product
General		
organic chemistry	104–106	<1–5
Fine organic chemistry	102–104	from 5 up to >50
Pharmaceutics	10–103	from 25 up to >100

The use of the method of interphase catalysts (IPC) in two-phase liquid systems allows one to ensure raw material, energy and human resource saving [1].

Increasing attention to this area of catalysis is to a high extent due to the development of a large number of polyoxometallate (POM) homogeneous catalysts and discovery of catalytic systems based on peroxopolyoxometallates

(PPOM) used in combination with the catalysts of inter-phase transfer – quaternary ammonium salts (QAS) [2–6]. These catalytic systems, for example $Q_3\{PO_4[MO(O_2)_2]_4\}$ or $Q_2\{HPO_4[MO(O_2)_2]_2\}$ etc., allow developing new efficient approaches to the synthesis of a number of practically valuable aliphatic and aromatic epoxides, as well as monocarboxylic (RCOOH) and dicarboxylic ($HOOC(CH_2)_nCOOH$) acids through the direct oxidation of various organic substrates by hydrogen peroxide (Fig. 1).

The complexes of molybdenum and tungsten are successfully used in the reactions involving oxidation of organic compounds for a long time [8]. By present, many processes of the oxidation of organic compounds have been developed with the aqueous solutions of 10–35 % H_2O_2 as oxidizing agent in the presence of peroxo-complexes (for example, of tungsten) formed under the conditions *in situ* in the systems: $H_2O_2-H_3PO_4-Na_2WO_4$ [3], $H_3PW_{12}O_{40}-H_2O_2$ [4] or $H_2O_2-Na_2WO_4-$



$\text{R}^1 = -(\text{CH}_2)_n\text{CH}_3$; $\text{R}^2 = -(\text{CH}_2)_n\text{COOH}$;

$\text{R}^3 = -(\text{CH}_2)_n\text{CH}_3$ or Ar

M = Mo, W etc.

Q = $[\text{Bu}_4^{\text{n}}\text{N}]^+$, $[\text{MeN}(n\text{-C}_8\text{H}_{17})_3]^+$, $[\text{C}_5\text{H}_5\text{NCet}]^+$ etc.

Fig. 1. Scheme of the oxidation of organic substrates [7].

$\text{NH}_2\text{CH}_3\text{PO}_3\text{H}_2$ [5]. The catalysts of interphase transfer are QAS of chloride, fluorine, bromine or hydrosulphate, containing alkyl groups $\text{C}_4\text{-C}_{18}$ or cations of the type $[\text{C}_5\text{H}_5\text{N-C}_{16}\text{H}_{33}]^+$. It is known that a mixture of peroxopolyoxocomplexes of tungsten including those catalytically inactive is formed under *in situ* conditions.

Taking into account the continuing debates concerning the structure of active oxidizing particles that participate in oxidation of organic substrates by hydrogen peroxide, we must stress that the degree of metal oxidation remains unchanged in the case of peroxometalate mechanism, and stoichiometric oxidation does not occur in the absence of H_2O_2 . Quite contrary, in the case of the reaction follows the oxometalate route, the degree of metal oxidation changes; in the absence of H_2O_2 , when the catalyst is in the oxidized form, stoichiometric oxidation is observed [9].

It should be kept in mind that peroxometalate mechanism is characteristic of transition metals [9a, b, c] which are relatively weak oxidizers, for example Mo(VI), W(VI), Ti(IV), Re(VII). For transition metals that are strong oxidizers in the highest oxidation degrees, for example Cr(VI), Mn(V), Os(VIII), Ru(VI), Ru(VII), oxometalate mechanism is observed. Vanadium (V) may catalyse oxidation depending on substrate, either *via* the peroxometalate mechanism (olefin epoxidation) or *via* oxometalate mechanism (oxidation of alcohols).

As far as tungsten complexes are concerned, it should be noted that according to the available data these catalytic complexes are in solution most probably in the poly-core state, presumably in the two-core (W_2) or four-core (W_4),

depending on preparation conditions [3a, 4a]. The authors of [3a] synthesized and isolated individual four-core complex in the crystalline form; its structure was established by means of single crystal diffractometry. Unfortunately, the authors presented incomplete structural data.

The four-core structure of similar complexes can be also assumed relying on the data for molybdenum peroxo complex [10], which is a crystallochemical analogue of tungsten. The structural data for the complex anion $\{\text{PO}_4\{\text{MoO}(\text{O}_2)_2\}_4\}^{3-}$ were published in full.

The first attempt to use EXAFS in combination with Raman and IR spectroscopy to reveal the state (local structure) of tungsten peroxo complexes in reaction solutions was made in [11].

The major results of the investigation of structural characteristics of the formed peroxo complexes for $[\text{Bu}_4^{\text{n}}\text{N}]_3\{\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4\}$ as example and the data of the tests of synthesized complex compounds of tungsten as catalysts for the reactions of oxidation of various organic substrates are described in the present work.

INVESTIGATION OF THE STRUCTURE OF PEROXO COMPLEXES AT DIFFERENT STAGES OF THE SYNTHESIS OF TETRA(DIPEROXO-TUNGSTEN)PHOSPHATE-TETRA-N-BUTYLAMMONIUM

Experimental

Precursors of peroxopolyoxocomplexes ($\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$, "kh. ch." reagent grade, $[\text{Bu}_4^{\text{n}}\text{N}]\text{Cl}$ ($\geq 95\%$, Acros) and catalytic systems (PPOM) for $[\text{Bu}_4^{\text{n}}\text{N}]_3\{\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4\}$ complex as example were studied using EXAFS, Raman and IR spectroscopy.

X-ray spectra of the L_3 edge of tungsten absorption were recorded at the EXAFS station of the Siberian Centre for Synchrotron and Terahertz Radiation (Novosibirsk) using a standard procedure [12] for transmission. The spectra were recorded with the electron energy in VEPP-3 storage equal to 2 GeV, and current 80 mA. The spectrometer has a two-crystal split monochromator Si (111) and proportional chambers as detectors.

For all samples, the oscillating part of EXAFS spectra of $(\chi(\mathbf{k}))$ function was analysed

in the form of $k^2\chi(\mathbf{k})$ within the wavenumber range $k = 3.0\text{--}14 \text{ \AA}^{-1}$. The isolation of the oscillating part of absorption coefficient and modelling of the spectra in order to determine structural data were carried out with the help of Viper software [13]. The quantum chemical parameters for modelling were calculated using the software package FEFF-7 [14].

Solid samples were analysed in the form of tablets with polypropylene (fraction $<0.25 \text{ mm}$) with the thickness providing tungsten content 20 mg/cm^2 . The solutions were placed into tight cells with the windows made of polyethylene; tungsten concentration in solution was 0.1 mol/L .

The Raman spectra of solid samples and their solutions within the range $100\text{--}3600 \text{ cm}^{-1}$ were recorded with a RFS 100/S Raman-Fourier spectrometer (Bruker). The source of excitation was an Nd-YAG laser ($\lambda = 1064 \text{ nm}$), with radiation power 400 mW .

Results and discussion

In general, a comparison between the curves of radial distribution of atoms (RDA) around tungsten in the process of preparation of the individual complex $[\text{Bu}_4^{\text{n}}\text{N}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$ (Fig. 2) points to the fact that two major types of changes occur in the structure of phosphotungstic acid ($\text{H}_2\text{PW}_{12}\text{O}_{40}$) when it is used as a precursor for the synthesis of peroxo complex. First of all, the core number of the complex decreases; initially it is a W_{12} structure; $\text{W}\text{--}\text{W}$ distance remains almost unchanged and is about 3.6 \AA . Second, the symmetry of the oxygen surroundings of tungsten changes. In all the cases, in het surroundings of a tungsten atom there is one oxygen atom that is connected with tungsten through a double bond (with a distance of $1.64\text{--}1.74 \text{ \AA}$). In addition, a group of distances in the region of $1.9\text{--}2.0 \text{ \AA}$ was observed, corresponding to peroxo groups attached to tungsten. Both these groups are well expressed in RDA curves as peaks. However, the distances in the region of $1.9\text{--}2.0 \text{ \AA}$ run into one peak as a consequence of the insufficient resolution of the method. Peak intensities change as a consequence of changes of the symmetry of tungsten surroundings, with the conservation of total coordination number which is equal to six.

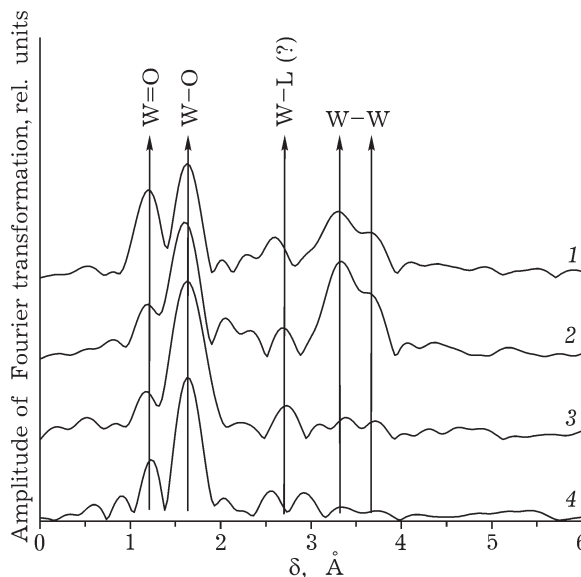


Fig. 2. RDA curves of tungsten for K edge for the samples: 1 - $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in the solid phase; 2 - aqueous solution of $0.17 \text{ M H}_3\text{PW}_{12}\text{O}_{40}$; 3 - reaction mixture (aqueous solution of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ with the addition of a 30 % aqueous solution of H_2O_2 , $[\text{H}_2\text{O}_2]/[\text{H}_3\text{PW}_{12}\text{O}_{40}] = 200$); 4 - filtrate after the isolation of the complex salt $[\text{Bu}_4^{\text{n}}\text{N}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$ [11].

It is most difficult to establish the nature of the peak with a distance in the region of 3.3 \AA . This peak is present in all the samples and can be interpreted either as the distance between $\text{W}\text{--}\text{O}$ or as the $\text{W}\text{--}\text{P}$ distance. It should be noted that two-core complex anions W_2 contain at least two non-equivalent tungsten atoms differing in the structure of the surroundings. The solution of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ oxometallate with H_2O_2 may contain either two-core tungsten complexes or more complicated formations arising due to coordination of two-core particles with PO_4^{3-} groups that are present in solution. The possibility of the formation in this solution and the existence in equilibrium for a series of tungsten peroxo complexes was stressed previously by us and other researchers [3, 4, 6].

For the problems of catalysis, the item of interest is the coordination of two-core residues with PO_4^{3-} groups; this is why we separated the formed complexes with the help of $\text{Bu}_4^{\text{n}}\text{NCl}$. We isolated the complex $[\text{Bu}_4^{\text{n}}\text{N}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$ from solution. This complex includes phosphorus-containing fragments. The mother solution was the subject of

further studies. Among the elements that can be observed by means of EXAFS, only tungsten and oxygen are present in this solution. On this basis, interpretation of the spectrum was carried out. In addition, the conservation of the position and shape of the peak corresponding to the W-W distance in $\text{PW}_{12}\text{O}_{40}^{3-}$ anion allowed us to assume that in the sample under analysis (Fig. 3) it corresponds to the W-W distance, too.

It follows from the data shown in Fig. 3 that the chosen model of structure leads to a good reproducibility of the peak in the region of interest. The set of coordination spheres with interatomic distances and coordination numbers, obtained as a result of modelling, corresponds to the structure of a two-core anion $[\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2]^{2-}$. So, after the removal of phosphorus-containing $[\text{Bu}_4^n\text{N}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$ complex from solution, a two-core anion $[\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2]^{2-}$ remains in the solution. This result agrees with the data reported in [6] describing the isolation of a salt from the mother solution by adding KCl in excess during the synthesis of $\text{Cet}_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$. According to the data reported in [15, 16], the IR spectrum of this salt (absorption bands, cm^{-1} : 965, 952 (shoulder), 835, 767, 616, 566, 552) corresponds to the spectrum of the complex salt $\text{K}_2[\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$.

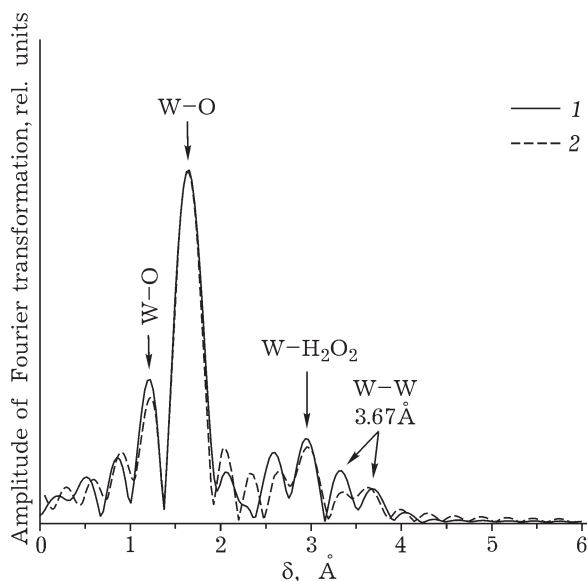


Fig. 3. RDA curves around tungsten for the sample of mother solution: 1 - experimental, 2 - calculated [11].

Relying only on the EXAFS data, we may state that the basis of the isolated complex $[\text{Bu}_4^n\text{N}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$ is formed by two-core groupings $\{[\text{WO}(\text{O}_2)_2]_2(\eta^1, \eta^2-\text{O}_2)_2\}$. However, it is impossible to establish unambiguously whether these fragments are coordinated at phosphorus atom with the formation of a four-core anion. This problem may be solved with the help of Raman spectroscopy. According to the data reported in [10], the Raman spectra of various peroxy complexes differ from each other notably. So, Raman spectroscopy can be used to identify the structure of these complexes. The spectra of the isolated complex $[\text{Bu}_4^n\text{N}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$ in the solid form and as a solution in acetonitrile are shown in Fig. 4. The spectra of the solid salt $[\text{Bu}_4^n\text{N}]\text{Cl}$ and pure acetonitrile are shown in the same Figure, too.

The spectrum of the solid complex $[\text{Bu}_4^n\text{N}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$ contains, in addition to the lines related to the vibrations of the cation, also the lines connected with the vibrations of various fragments of the peroxy complex: 979 ($\nu(\text{W}=\text{O})$), 859 ($\nu(\text{O}-\text{O})$), 652, 593, 575 and 533 ($\nu_{\text{as}}(\text{W}-(\text{O}_2))$ и $\nu_{\text{s}}(\text{W}-(\text{O}_2))$), as well as 390, 330, 299, 263 and 232 cm^{-1} . The latter bands are likely to relate to the bending vibrations of different fragments of the complex. The spectrum recorded by us coincides with the spectra of the complex with four-core structure

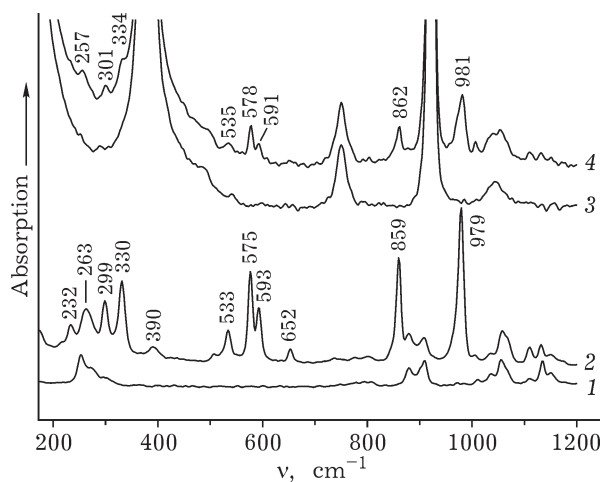


Fig. 4. Raman spectra: 1 - solid $[\text{Bu}_4^n\text{N}]\text{Cl}$, 2 - solid complex $[\text{Bu}_4^n\text{N}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$, 3 - CH_3CN , 4 - 0.1 M solution of complex $[\text{Bu}_4^n\text{N}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$ in acetonitrile [11].

reported in [3b]. Unfortunately, the lines directly related to the vibrations of $\{\text{PO}_4\}$ fragment cannot be recorded in the spectra because of their low intensity. The frequencies of these vibrations would allow us to establish unambiguously whether this complex is two-core (W_2) or four-core (W_4). On the other hand, the absorption bands in the IR spectrum of this complex relating to the vibrations of this fragment are rather intense [6].

In the IR spectrum of the complex with the Raman spectrum identical to the recorded one, absorption bands at 1085, 1052 and 1038 cm^{-1} are observed. They relate to $\nu_{\text{as}}(\text{PO}_4)$ vibrations [6]. The position and the number of these bands point to the fact that the complex contains $\{\text{PO}_4\}$ fragment and its symmetry is lower than C_{3v} ; this agrees with the structure of anion $(\mu_4\text{-PO}_4)\{\text{WO}(\text{O}_2)_4(\eta^1, \eta^2\text{-O}_2)_4\}^{3-}$ proposed in [3b]. It is necessary to stress that in the case of solution of the complex in acetonitrile, the analysis of the region 1100–1000 cm^{-1} in the IR spectrum of the complex is impossible because of the strong absorption by the solvent. At the same time, the lines related to the vibrations of $[\text{Bu}_4^{\text{n}}\text{N}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$ complex are well seen in the Raman spectrum of acetonitrile (see Fig. 4). The positions of lines, their relative intensities their number in the Raman spectrum of the solution of this complex in acetonitrile almost completely coincide with the parameters of the spectrum of $[\text{Bu}_4^{\text{n}}\text{N}]_3\text{Cl}$ in the solid state (see Fig. 4, curve 1). The shifts of frequencies do not exceed 5 cm^{-1} , which can be explained by the difference in intermolecular interactions in the solid phase and in acetonitrile solution. Therefore, the four-core structure of peroxo complex $[\text{Bu}_4^{\text{n}}\text{N}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$ is conserved in acetonitrile solution.

As a result of the investigation of structural characteristics of the major polyoxo and peroxopolyoxo complexes of tungsten, formed in the interaction of the aqueous solutions of phosphotungstic heteropolyacid and hydrogen peroxide, the following was established with the help of EXAFS, Raman and IR spectroscopy:

– as a result of their interaction, the number of cores in the formation complexes decreases with respect to the precursor $\text{H}_3\text{PW}_{12}\text{O}_{40}$;

– the symmetry of the oxygen surroundings of tungsten changes while the distance W–W is conserved;

– after the removal of $[\text{Bu}_4^{\text{n}}\text{N}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$ complex from solution, a two-core anion $[\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2]^{2-}$ remains in the solution.

Taking into account the obtained results and the available literature data on the fact that the highest catalytic activity is exhibited by the complex anion of the composition $\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{3-}$, a series of catalysts containing exactly this anion were synthesized. The syntheses of catalytic complexes $[\text{Bu}_4^{\text{n}}\text{N}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$, $[\text{Me}(n\text{-C}_8\text{H}_{17})_3\text{N}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$, $[\text{C}_5\text{H}_5\text{NCe}t_3]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$ and $[\text{Et}_2\text{Bn}_2\text{N}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$ were carried out according to the procedures described in [6] using the QAS of fluorine and chlorine for the synthesis.

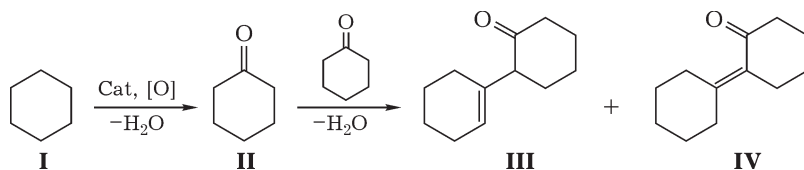
CATALYTIC OXIDATION OF ORGANIC SUBSTRATES

The synthesized catalytic complexes $[\text{Bu}_4^{\text{n}}\text{N}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$ were tested in the oxidation of various organic substrates by hydrogen peroxide using the IPC method.

Experimental

Oxidation was carried out in a shaken reactor of the type of catalytic duck (300–400 double swaying/min) equipped by a backflow condenser and a jacket for thermostating. Reaction temperature was maintained with the help of an aqueous thermostat with the accuracy of ± 1.0 °C.

Analysis of substrates and reaction mixtures was carried out with Saturn 2000 instrument (Varian) by means of gas chromatography-mass spectrometry with ion trap. Chromatographic separation was carried out using a quartz capillary column 30 m long with the inner diameter of 0.25 mm, NZhF CP-Sil 24 CB with temperature control from 50 to 250 °C (7 °C/min), evaporator temperature was 300 °C. Normalization according to [17] was used. The current control over substrate conversion was carried out by means of TLC on Sorbfil or Silufol plates on silica gel using proper eluents.



Scheme 1. Catalytic oxidation of cyclohexane by atmospheric oxygen.

Identification of compounds was performed by means of gas-liquid chromatography using authentic samples from Aldrich, and by means of NMR spectroscopy. The NMR spectra were recorded with a Bruker AC-200 instrument in CDCl_3 (working frequency 200.13 MHz for ^1H , 50.32 MHz for ^{13}C). The signal of chloroform was used as the internal standard (δH 7.24 ppm, δC 76.90 ppm).

Oxidation of α,β - and β,γ -unsaturated cyclic ketones

In the known industrial processes of the synthesis of caprolactam, adipinic acid and other compounds, a complicated multicomponent mixture is formed at the stage of liquid-phase catalytic oxidation of cyclohexane **I** (Scheme 1). Along with the major product **II**, as a result of cyclohexanone dimerization, α,β - and β,γ -unsaturated cyclic ketones are formed: 2-(1-cyclohexenyl)-1-cyclohexanone **III** and 2-cyclohexylidene-1-cyclohexanone **IV** are formed. These compounds are incorporated into the light fraction which is obtained by distillation of X-oil under vacuum [18]. The amount of these side products is 80 to 100 kg per 1 t of treated raw material **I**. Ketone **III** is thermodynamically unstable and isomerizes at 150 °C to form compound **IV**. Isomerization is an equilibrium process, so under usual conditions a mixture of isomers **III** and **IV** at a ratio of 90 and 10 %, respectively, will be formed [18, 19].

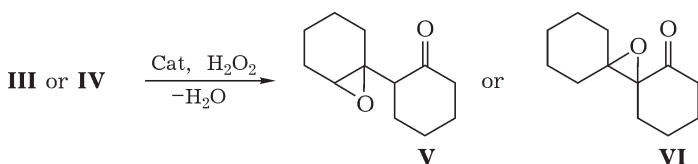
The proposed approach involving IPC for the catalytic oxidation of cyclic ketones **III**, **IV** (having unsaturated C=C bonds) by hydrogen peroxide (Scheme 2) can be used to obtain epoxide

oxides: 2-(7-oxabicyclo[4.1.0]hept-1-yl)cyclohexanone **V** and 13-oxadispiro[5.0.5.1]tridecan-1-one **VI** [19].

A mixture (with the density of 1.1 g/cm³) isolated by vacuum distillation from the light fraction of X-oil from cyclohexanone production (Azot Co., Kemerovo) was used as the substrate. Dichloroethane was used as a solvent.

Experiments on the catalytic oxidation of the substrate containing a mixture of ketones **III**, **IV** revealed the difference in the catalytic activity of two tested peroxopolyoxotungstate complexes depending on the used catalyst of interphase transfer [20, 21]. The most active catalytic system was found to be $[\text{C}_5\text{H}_5\text{NCet}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$ – tetra(oxodiperoxotungstato)phosphate of *N*-hexadecylpyridinium. In the presence of this catalytic system, it is possible to obtain epoxide 13-oxadispiro[5.0.5.1]tridecan-1-one **VI** with the yield of 73 %, with the degree of **III** and **IV** conversion equal to 90 and 55 %, respectively. Decreased activity of the catalyst $[\text{Bu}_4^+\text{N}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$ agrees with lower lipophilicity of $[\text{Bu}_4^+\text{N}]^+$ as the agent of inter-phase transfer in comparison with *N*-hexadecylpyridinium.

In general, it was established that the oxidation of 2-cyclohexylidene-1-cyclohexanone **IV** by hydrogen peroxide in the presence of a bifunctional catalyst $[\text{Bu}_4^+\text{N}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$ or $[\text{C}_5\text{H}_5\text{NCet}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$ proceeds with the formation of epoxide 13-oxadispiro[5.0.5.1]tridecan-1-one **VI**. Oxidation of 2-(1-cyclohexenylidene)-1-cyclohexanone by hydrogen peroxide in the presence of the indicated catalysts will proceed



Scheme 2. Catalytic oxidation of cyclic ketones.

mainly with the formation of 1,2,3,4,6,7,8,9-octahydrodibenzo[*b,d*]furan and cyclopentanoic acid.

So, the reactions of the oxidation of α,β - and β,γ -unsaturated cyclic ketones by hydrogen peroxide may proceed in one technological stage under soft conditions (atmospheric pressure, temperature 55–65 °C), with low catalyst concentrations ($[\text{Sub}]/[\text{Cat}] = 200$) with the formation of useful and valuable products from the wastes of caprolactam production – the light fraction of X-oil: epoxides, dibenzofuran derivatives and carboxylic acids.

Oxidation of unsaturated fatty acids and their esters of plant origin

Potential possibilities of the use of the products of plant origin in organic synthesis are far from being exhausted by the existing area of their application. This is first of all true for unsaturated fatty acids isolated in large amounts from coniferous, foliferous, landscape and cultivated plants. The most interesting reactions from the practical point of view are those involving oxidation of double bonds (C=C) of the indicated compounds, resulting in the formation of new compounds, including optically active ones.

One of the sources of unsaturated fatty acids is tall oil formed from wood processing. Tall oil is a valuable source of resin acids (colophony). In addition, they contain free unsaturated fatty acids (35–37 %): oleic, linolic, linolenic. Oleic (*cis*-9-octadecenic) acid accounts for about 80 % of the total amount of indicated acids [22, 23].

As a result of investigations [24, 25] aimed at determination of the optimal conditions for the oxidation of *cis*-9-octadecenic acid by hydrogen peroxide in a two-phase system involving the catalytic systems based on peroxopolyoxotungstate (Scheme 3), the following was established:

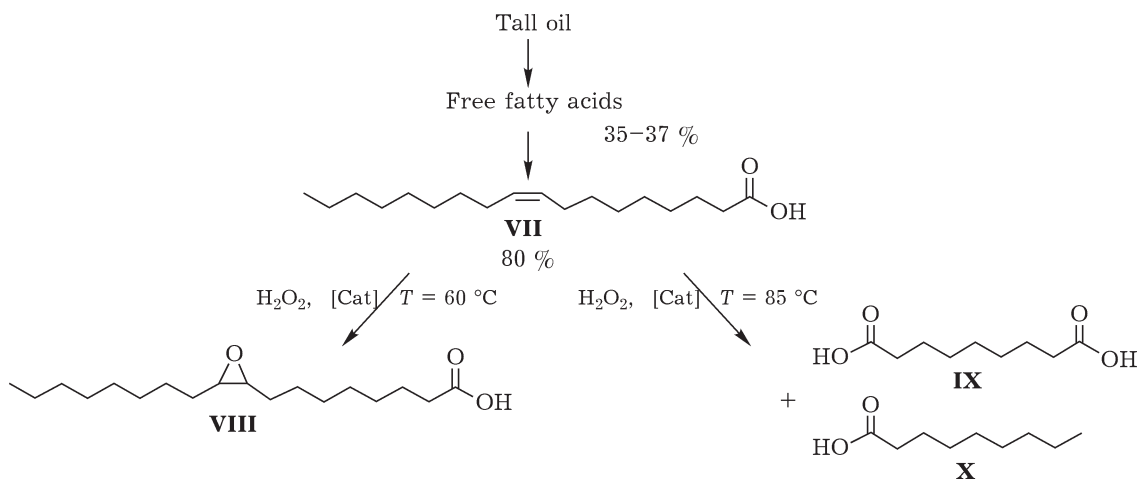
- in the reactions of epoxidation and oxidative splitting, the highest activity among the tested catalytic complexes $[\text{Bu}_4^+\text{N}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$, $[\text{Me}(n\text{-C}_8\text{H}_{17})_3\text{N}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$, $[\text{C}_5\text{H}_5\text{NCet}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$ is exhibited by tetra(di-peroxotungsto)phosphate of methyltri-*n*-octylammonium;

- the best result is observed for the ratio $[\text{Cat}]/[\text{Sub}]/[\text{H}_2\text{O}_2] = 1 : 1000 : 2000$; within temperature range 50–60 °C the reaction proceeds within 5–7 h with conversion degree 95 %, the resulting reaction mixture contains *cis*-9,10-epoxyoctadecenic acid **VIII** up to 90 % and about 5 % of the products of oligomerization and hydrolysis of oxiran group;

- epoxidation of *cis*-9-octadecenic acid **VII** by hydrogen peroxide can be carried out within organic solvent (the same results were obtained for reactions carried out in chloroform, 1,2-dichloroethane, and without any solvent);

- epoxidation of *cis*-9-octadecenic acid **VII** by hydrogen peroxide in the absence of catalyst, other conditions being the same, can lead only to 5 % yield of epoxide **VIII** along with the formation of high molecular mass products of peroxide oxidation in large amounts [26].

The chosen catalyst was tested in oxidative splitting of **VII** by a 35 % solution of hydro-



Scheme 3. Catalytic oxidation of oleic acid **VII** by hydrogen peroxide.

gen peroxide. It was established that it is necessary to rise temperature to 85 °C and increase catalyst concentration not less than by a factor of 2 to achieve high conversion degree (95 %) and selectivity (95–96 %). As a result, 1,7-heptanedicarboxylic (azelaic) **IX** and *n*-nonanic (pelargonic) **X** acids are formed (see Scheme 3).

Another interesting subject for oxidative functionalization of natural compounds in order to obtain precursors of medical preparations is (9*Z*,12*R*)-12-hydroxyoctadec-9-enic (ricinoleic) acid **XI**. Due to its availability (it is present in triglycerides of castor oil) and the asymmetric *R* centre in position 12, it is a promising synthon for obtaining chiral polyfunctional compounds (Scheme 4). On the basis of ricinoleic acid, the compounds possessing antitumour, antiviral, antiulcer and antidiabetic activity were obtained [27].

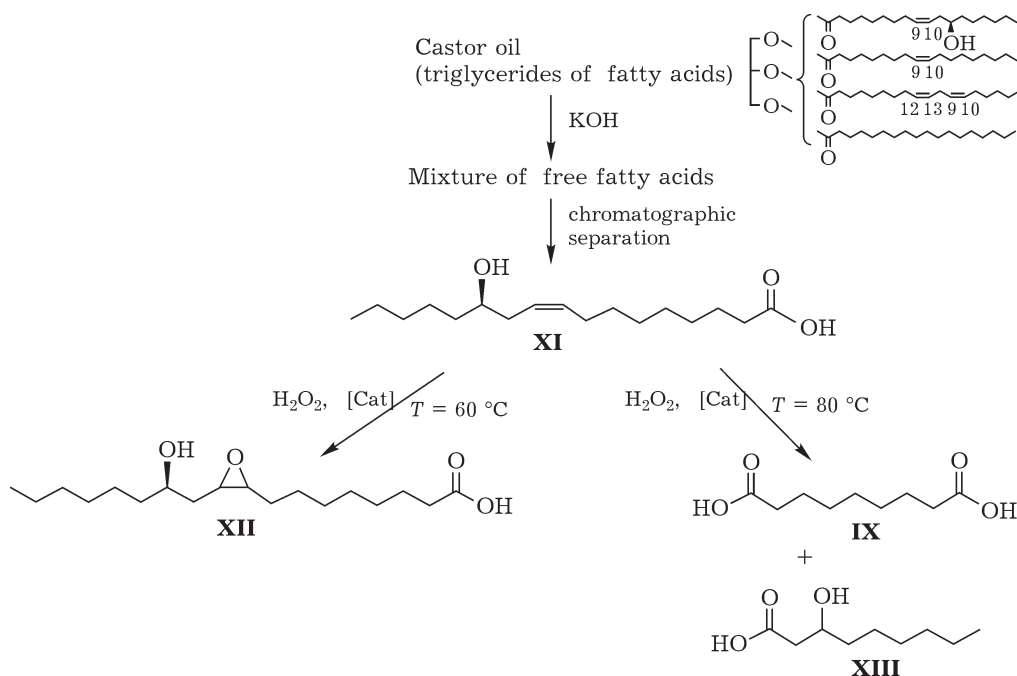
Ricinoleic acid **XI** under the conditions of oxidative splitting of **VII** with the selectivity of 84 % turns into acids **IX** and 3-hydroxynonan-ic **XIII**; along with these products, it also forms about 4 % of 12-hydroxy-9,10-epoxyoctadecanoic acid **XII**.

The determined optimal conditions for epoxidation of compound **VII** were successfully used to epoxidate ricinoleic acid, methyl esters

of oleic and ricinoleic acids. For example, for the ratio [Cat]/[Sub]/[H₂O₂] = 1 : 1000 : 2000 and temperature 60 °C, without organic solvents (substrate plays the part of organic phase) using catalyst [Me(*n*-C₈H₁₇)₃N]₃{PO₄[WO(O₂)₂]₄}, the epoxide of ricinoleic **XII** was obtained with conversion degree 93 % and selectivity 84 %. The yield of methyl ester of epoxyoctadecanoic acid was 85 %, with conversion degree 94 %, while epoxidation of methyl ester of ricinoleic acid proceeded with the conversion degree of 96 % and selectivity 87 %.

Oxidation of betulin and betulin diacetate

The most readily available triterpenoids of lupane series possessing diverse biological activity include betulin and its derivatives. The concentration of betulin in the external bark of birch exceeds 30 % of bark mass. Betulin derivatives exhibit clearly pronounced anti-HIV, hepatoprotective, antiulcer, anti-inflammatory, wound-healing and immunomodelling activity, and antiarthritic action [28]. Because of this, the oxidation of betulin and its diacetate by 30 % solution of H₂O₂ under the conditions of IPC was studied for the purpose of obtaining epoxides of these compounds (Scheme 5).

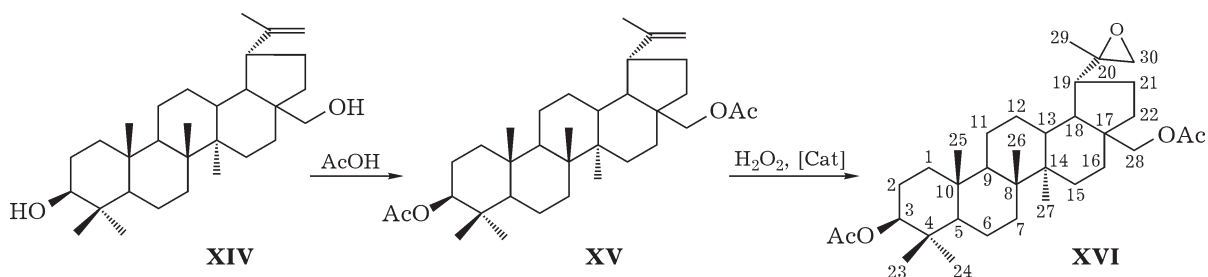


Scheme 4. Catalytic oxidation of ricinoleic acid **XI** by hydrogen peroxide.

The reactions were carried out in trichloroethylene using a 35 % solution of H_2O_2 at a temperature of 70 °C and the ratio $[\text{Sub}]/[\text{Cat}] = 30$ и $[\text{H}_2\text{O}_2]/[\text{Sub}] = 18$. It was determined that the most efficient catalyst under these conditions is a complex with methyltri-*n*-octylammonium $[\text{Me}(n\text{-C}_8\text{H}_{17})_3\text{N}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$. The use of the catalytic system with this cation leads to a 100 % conversion of betulin **XIV**, with using $[\text{C}_5\text{H}_5\text{NCet}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$ the transformation of betulin proceeds only by 80 %; with the catalyst $[\text{Bu}_4^+\text{N}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$ conversion degree did not exceed 50 %. In all the cases, a mixture of several oxidation products in comparable amounts was formed in the reaction mixture. The absence of selectivity in the reaction under study is due to the presence of at least three most probable positions for oxidative modification of molecule **XIV**. In this connection, to study the conditions of oxidation of unsaturated carbon-carbon bond, betulin diacetate was used as a substrate.

Betulin diacetate **XV** was obtained directly from birch bark using a new method based on the integration of the stages of betulin isolation from betulin-suberine complex of birch bark and its acylation under boiling of ground bark in acetic acid [29]. The initial raw material was the external bark of *Betula pendula* Roth., sampled near Krasnoyarsk.

Oxidation of **XV** was carried out in chloroform solution by 35 % hydrogen peroxide in the presence of $[\text{Me}(n\text{-C}_8\text{H}_{17})_3\text{N}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$ at a temperature of 60 °C. It was established that 98 % betulin diacetate conversion degree is achieved after 4 h of the start of reaction. Epoxide of betulin diacetate **XVI** is formed as reaction product with the selectivity of 90 %.



Scheme 5. Synthesis of betulin diacetate epoxide **XVI**.

The product was isolated from the reaction mixture by recrystallization from ethanol and identified on the basis of NMR data (NMR ^1H , ^{13}C).

In the general form, the mechanism of two-phase hydrogen peroxide oxidation of organic substrates containing unsaturated carbon-carbon bonds is presented in Fig. 5. The reaction preferentially proceeds in the organic phase through the transport of oxygen from peroxy complex to the substrate. Subsequent regeneration of peroxy complex by hydrogen peroxide takes place at the interface. It should be stressed that the catalytic activity of the complex $\text{Q}_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$ is substantially affected by the nature of the quaternary cation Q. In the case when oxidation is carried out without organic solvents and the role of organic phase is played by the substrate, the necessity to isolate the catalyst from the reaction medium is eliminated. The formed products, for example carboxylic acids, as a rule, are well soluble in water, and their isolation may be carried out from preliminarily decanted aqueous phase. The catalyst thus remains in the organic phase. Subsequent cycles of product formation are carried out by adding new portions of the substrate and the solution of the oxidizer.

CONCLUSIONS

The IPC method promoted the success of modern organic synthesis in the area of the so-called green chemistry. In this work we demonstrated the possibilities of the use of bifunctional catalysts possessing the properties of metal complex and interphase catalysts.

Using this approach, the possibility to obtain useful and valuable products was demon-

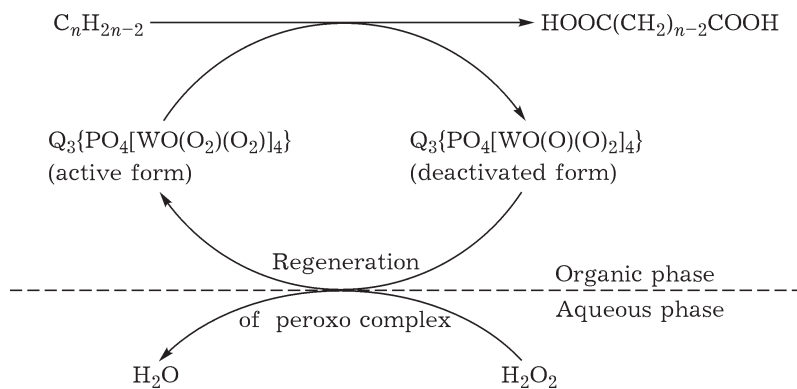


Fig. 5. Scheme of the mechanism of oxidation of organic substrates by hydrogen peroxide in two-phase systems.

strated: epoxides, mono- and dicarboxylic acids from the wastes of caprolactam production (the light fraction of X-oil); the side products of wood processing (tall oil); biologically active components of renewable raw material, extractable from castor oil, birch bark etc.

In future, it may be expected that the demand for epoxides and carboxylic acids obtained from plant raw material would only increase. The indicated compounds belong to small-scale products; the sufficient amounts of them at the home market define the sustainable development of such branches as the development of new medical preparations and materials with required properties, including those for the military industrial complex.

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