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**ABSTRACT**

of the dissertation for the degree of Doctor of Philosophy

**OXIDATION OF C<sub>2</sub>-C<sub>3</sub> ALKENYL AROMATIC  
HYDROCARBONS AND PYROCONDENSATE WITH  
HYDROGEN PEROXIDE**

Speciality: 2314.01-Petrochemistry

Field of science: Chemistry

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The work was performed at the laboratory of "Alicyclic compounds" of the Institute of Petrochemical Processes named after academician Y.H.Mammadaliyev, Azerbaijan NAS.

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## GENERAL DESCRIPTION OF WORK

**Relevance of the work.** Introduction of various oxygen-containing functional groups to the composition of saturated and unsaturated hydrocarbons and the development of new effective catalytic systems for the implementation of these processes are one of the important directions of modern petrochemistry.

It is known that mainly two general directions of the conversion of substrates are chosen for the introduction of oxygen-containing functional groups (oxide, hydroxyl, carbonyl, carboxyl, etc.) into the composition of saturated and unsaturated hydrocarbons, as well as alicyclic: aerobic oxidation in the liquid phase<sup>1</sup> and electrophilic addition of oxygen functions with oxidizing agents such as peroxy acids, peroxides and hydroperoxides, hydrogen peroxide, etc. To achieve high selectivity for certain products the main direction of research is the choice of an effective and highly active catalytic system.

The implementation of the combined decomposition of ethylbenzene (or cumene) hydroperoxide and the epoxidation of propylene on an industrial scale with the participation of metals of VI-VIII groups opened a new direction in the field of oxygen functionalization of unsaturated hydrocarbons. This direction is still relevant<sup>2</sup>.

The research on the functionalization of unsaturated hydrocarbons involving hydrogen peroxide, the most environmentally friendly oxidizing agent and heterogeneous catalytic systems has been developing in recent years.

The first report on the use of these systems in large-capacity industrial processes appeared at the end of the twentieth century after the development of a process for producing pyrocatechol and

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<sup>1</sup> Sheldon, R.A. Metal-Catalyzed Oxidations of Organic Compounds/ R.A. Sheldon, J.K. Kochi // Academic Press, -New York, -1981, - p. 418. p.456

<sup>2</sup> Alimardanov, H.M. Catalytic oxidation of cyclic compounds to dicarboxylic acids. New perspectives. /H.M. Alimardanov, N.I. Garibov, M. Yu. Abdulaeva, E. T. Suleymanova // Processes of petrochemistry and oil refining. -2012, No. 1, p. 37-62.

hydroquinone from phenol with the participation of microporous titanium silicalites by Enichem company (Italy). Metal-carbon systems and mesoporous silicates are currently offered for the oxidation of various hydrocarbons and their derivatives.

However, the use of these systems in the oxidation of macrocyclic unsaturated and alkenyl aromatic hydrocarbons is episodic in nature. There are few works in this direction, although such compounds as phenyloxirane, macrocyclic epoxides are valuable products of petrochemical and fine-organic synthesis and used to produce pharmaceutical, aromatic, biologically active compounds, in the production of epoxy resins and plasticizers as well as fuel components.

### **Object and subject of research.**

For investigation of the reaction of liquid-phase catalytic oxidation, the following compounds were used as the initial compounds of the study: cyclododecene, pyrocondensate, styrene,  $\alpha$ - and  $\eta$ -methylstyrenes, and tetrahydroindene.

Based on polyoxotungstate and cerium nitrate, new catalytic systems have been prepared in various ratios, and their activity has been studied in the reactions of epoxidation of styrene, its methyl derivatives, cyclododecene, tetrahydroindene, and fraction 130-190 °C of pyrocondensate to obtain an oxidate proposed as an anti-smoke additive. The choice of these hydrocarbons is due to the practical usefulness of the obtained epoxides as intermediates and synthons in the synthesis of biologically active compounds, drugs and fragrances, as well as the fractions 130-190 °C pyrocondensate to obtain oxidate, proposed as a smoke control additive.

**The aim of the work.** The aim of the thesis is to develop a process for producing oxygen-containing compounds, specially oxiranes and diols with aromatic and macrocyclic fragments or aromatic aldehydes; the development of effective catalytic systems based on REE and polyoxytungstate for the oxidation of styrene and its methyl derivatives of  $\alpha$ - and  $n$  -methylstyrene, *p*-methylstyrene, and also cyclododecene, THI and pyrocondensate. Establishing a correlation between the yields of the target products and the nature of

the catalyst, as well as the structure of the starting hydrocarbons and the reaction condition.

The task of the dissertation was as follows:

- ✓ synthesis of REE-containing heterogenized samples of polyoxotungstates and selection of effective, active catalysts in the epoxidation of styrene and its methyl derivatives, as well as cyclododecane.
- ✓ study of the physicochemical properties of the synthesized catalysts by various physical methods (IR, EPR, SEM, XRD, etc.).
- ✓ establishing the influence of the main factors on the electrophilic attachment of the active oxygen atom of the intermediate peroxocomplex to the double bond of the substrate and finding optimal conditions for the selective oxidation of alkenyl benzenes and cyclododecane to epoxides and aldehydes, respectively.
- ✓ obtaining oxygenate by oxidation of the pyrolysis condensate fraction separated from the products of pyrolysis of hydrocarbons in order to develop recommendations for their use as fuel components.

**Research methods.** During the dissertation work, the compositions and structures of the synthesized catalysts and reaction products were studied using IRS, NMR, EPR, GLC methods and X-ray phase analysis. In order to study the mechanism of the epoxidation reaction of styrene and its alkenyl derivatives, kinetic research methods were used.

**The main provisions submitted to the defence:**

- -results of catalytic oxidation of styrene and its methyl derivatives with hydrogen peroxide or it's adduct with urea (hydroperite);
- -the synthesis of polyoxotungstates modified with rare earth elements and the results of their physicochemical analyzes, the study of their activity and selectivity in the processes of obtaining the corresponding epoxides and aldehydes;

- -results of oxidation of representatives of macro-and polycyclic unsaturated hydrocarbons, cyclododecene, tetrahydroindene in the presence of selected ceriumpolyoxotungstate catalysts;
- - results of studies of the dependence of the oxidation of the above hydrocarbons on their structure
- -oxidation of the pyrocondensate extracted from the products of the pyrolysis process under the optimal conditions found and the results of testing the resulting oxygenate.

**Scientific novelty of the work.** A scientific direction has been developed and formulated in the chemistry of oxidative selective functionalization of C<sub>2</sub>-C<sub>3</sub> alkenyl aromatic hydrocarbons, which consists in the production of epoxides, diols and aldehydes under the conditions of inducing electrophilic reagents.

A relationship was found out between the activity of heterogeneous catalysts and the nature of the selected carriers using various analysis methods. It was found out that the selected catalytic systems exhibit high catalytic selectivity at the electrophilic addition of oxygen to a carbon-carbon double bond, however, high yields of oxiranes and aldehydes also significantly depend on the concentration of hydrogen peroxide and the nature of the solvent used in the oxidation of substrates.

Selected catalyst systems are also highly active in the oxidation of pyrocondensate to produce various oxygenates.

**Theoretical and practical significance of the research:**

- The theoretical foundations and experimental substantiation of the possibility of carrying out the reaction of liquid-phase oxidation of styrene and its methyl derivatives under conditions that meet the requirements of "green" chemistry with the participation of polyoxotungstates of the Keggin structure modified with rare-earth materials (Ce, Tb, Pr) homogeneous and heterogenized on highly dispersed carbon material can be used in industry for the production of various oxygen-containing multifunctional compounds.

- New highly efficient catalysts based on polyoxotungstate and REE oxides were developed and a selective method was proposed for the liquid-phase oxidation of alkenyl aromatic and macrocyclic unsaturated hydrocarbons to oxiranes and aldehydes.
- The synthesized catalytic systems were used in the oxidation of the 130-190 °C fraction of pyrocondensate isolated from liquid pyrolysis products, and obtained oxygenate was tested as a smoke additive in diesel fuel.
- A kinetic model of styrene oxidation, which is the basis of mathematical modeling and process optimization was obtained.

### **Personal contribution of the applicant.**

The solution of the problems posed in the dissertation, the preparation of catalysts, verification of their activity during the oxidation of substrates, the influence of various factors on the activity of the catalyst was carried out directly by the author. The resulting materials were processed personally by the author and presented in the form of reports and scientific articles.

In the context of some results, the author's share in experiments on the physical methods of catalysts has become predominant.

**Publications.** On the topic of the dissertation, 23 scientific papers were published: including 8 articles, 3 conference proceeding, 11 reports. The Patent of Azerbaijan has been received

### **Approbation and application of the work.**

The results of the dissertation were reported and discussed at the X International Conference "Mechanisms of Catalytic Reactions" Svetlogorsk, Kaliningrad Region, 2016; XXX International Scientific and Technical Conference dedicated to the memory of Academician of the Academy of Sciences of the Republic of Belarus Dilyus Lutfullich Rakhmankulov, Ufa, 2016; IX Baku International Mammadaliyev Conference on Petrochemistry 2016; IV International Scientific Conference of Young Researchers, 2016, Baku; at the II Russian Congress on Catalysis "ROSKATALIZ" Nizhny Novgorod, Novosibirsk 2017; 5th International School-

Conference on Catalysis for Young Scientists “Catalyst Design: From Molecular to Industrial Level” 20 May 2018 - 23 May 2018 Moscow, Russia; International Scientific and technical conference "Petrochemical synthesis and catalysis in complex condensed systems" dedicated to the 100th anniversary of academician B.K. Zeynalov 2017; International scientific conference "Actual problems of modern chemistry", dedicated to the 90th anniversary of the Institute of Petrochemical Processes named after Academician Yu.G. Mamedaliev. 2019.

**The name of the organization in which the dissertation work was performed.** The dissertation work was carried out in accordance with the research plan of the Institute of Petrochemical Processes of the Azerbaijan National Academy of Sciences.

**Structure of the dissertation.** The dissertation work consists of an introduction, 4 chapters, results, a list of cited scientific literature, including 148 references. The content of the work is presented on 150 pages of computer text containing 27 tables, 29 figures and 8 schemes. The presented thesis is 162138 characters. Introduction includes (11359 characters), chapter I (54252 characters), chapter II (13838 characters), chapter III (57969 characters), chapter IV (21842 characters), conclusions (2878 characters). Test reports are given in the form of an attachment.

In the introduction of the dissertation, the choice, relevance, purpose and tasks of the work are substantiated. Information about the scientific novelty and practical value of the dissertation is given.

**The first chapter** provides a literature review that discusses materials over the past 15-20 years on the oxidation of styrene, its various derivatives, as well as macrocyclic unsaturated hydrocarbons. The choice of the theme of the dissertation is justified in conclusion.

**The second chapter** is devoted to the synthesis of the starting compounds, the description of the experimental method and analysis of the prepared catalysts, oxidation products, as well as the determination of their physicochemical properties.

**The third chapter** contains the results of a study on the liquid-phase oxidation of styrene and its methyl derivatives. The results of kinetic studies of styrene oxidation with the participation of an aqueous solution of hydrogen peroxide are presented in a separate section. A kinetic model of the reaction has been compiled, which is recommended for mathematical modeling.

**The fourth chapter** presents the results of studies of the epoxidation and oxidative conversion of C<sub>9</sub>-C<sub>12</sub> macrocyclic unsaturated hydrocarbons and pyrocondensate with the participation of hydrogen peroxide and cerium polyoxytungstate. The effect of temperature and duration of the experiment on the conversion of THI and the composition of oxidation products are considered in a separate chapter. The influence of structural factors on the rate and direction of transformation of styrene, its methyl derivatives, as well as cyclododecene and tetrahydroindene is considered. A correlation was found between the structure of substrates and the direction of their transformation. Based on the tests the obtained oxygenate is recommended as an anti-smoke additive to diesel fuel.

In a separate section, the effect of temperature and duration of the experiment on the conversion of tetrahydroindene and cyclododecene, as well as on the composition of the oxidation products, is considered.

**In the conclusions**, the general results of the dissertation work are given and the main achievements of the research carried out are outlined.

## **MAIN CONTENT OF THE DISSERTATION**

### **1. Catalysts and research methodology**

An aqueous solution of hydrogen peroxide (GOST 10292-76) with a mass fraction of H<sub>2</sub>O<sub>2</sub> of 30-42.5% and a clathrate of hydrogen peroxide with urea (hydroperite) was used as an oxidizing agent of the above hydrocarbons.

Catalytic systems were synthesized by the interaction of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> or (NH<sub>4</sub>)<sub>10</sub>W<sub>12</sub>O<sub>41</sub> compounds and REE nitrates in the presence of an aqueous solution of oxalic acid, at a temperature

of 90-95°C, followed by evaporation and heating at 200-250 °C of the solution to form REE-containing HPC. The aqueous medium promotes the formation of condensed multinucleated anions in which hydroxy groups are completely absent, and the basis is M-O-M or M = O fragments. Anionic fragments of heteropoly compounds have regular geometric shapes and consist of  $[\text{MO}_6]^{6-}$  octahedra and  $[\text{MO}_4]^{2-}$  tetrahedra. Isopolyanions have voids between the octahedra where other heteroatoms, in particular, such cations of rare earth metals as Nd, Ce, La, Tb, Pr, etc., can successfully incorporate. HPC heteroatoms are located in tetrahedral or octahedral anion cavities, which are formed by the oxygen atoms of neighboring octahedra.

Catalysts for oxidation and epoxidation were also prepared by boiling aqueous solutions of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ ,  $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}$ , nitrates of REE and  $\text{H}_3\text{PO}_4$  in a predetermined amount for 5-6 hours. Then the solution was cooled to room temperature, filtered, evaporated at 110-120 °C and subjected to heat treatment at 220-250 °C for 2-3 hours and a solid mass of dark yellow was obtained. The catalyst was fed into the reaction mixture in the form of suspensions in formic or acetic acid.

The crystal structure of the synthesized catalytic systems was determined using an S-3400N scanning electron microscope with an Oxford Instruments Nano Analysis (OINA) microanalysis system.

The IR spectra of the catalyst samples were recorded on an Alpha IR Fourier spectrometer in the 400-4000  $\text{cm}^{-1}$  region or Vertex (Bruker) in the 100-700  $\text{cm}^{-1}$  region in the form of suspensions in liquid paraffin and tablets with KBr.

X-ray phase analysis was performed on a Miniflex diffractometer (Rigaku). Analysis with the calculation of interplanar distances calculated from  $2\theta$  values from the diffraction pattern showed the presence of  $\text{MPO}_4$ ,  $\text{M}[\text{PW}_{12}\text{O}_{41}]$  phases in the sample (where M = Ce, Pr, Nd)

To study the radical nature of the synthesized catalysts, the method of electron magnetic resonance (EPR) was used as the main physical method.

The consumption of  $H_2O_2$  was controlled by the method of permanganometry, and the amount of cyclododecene hydroperoxide was determined by the method of iodometry.

The composition and purity of the initial hydrocarbons, as well as the oxidation products, were determined by GLC analysis on a Color-500 chromatograph with a flame ionization detector column 2000×2 mm polyethylene glycol succinate (PGE) phase on chromosorb (5 wt.%), Helium carrier gas, column temperature 160°C, injector temperature 250 °C.

Chromatography-mass spectra were recorded on an Agilent Technologies GC 7890A-MSD 5975C instrument (HP5-MS column, temperature range from 40 to 280 °C with programmed heating, carrier gas-helium).

## **2. Oxidative conversion of styrene and its methyl derivatives with the participation of hydrogen peroxide in the presence of REE-containing polyoxotungstate catalysts**

An analysis of recent works shows that HPS based on polyvalent metals Co, Mo, and W modified with compounds of rare-earth elements (REE), whose atomic nuclei possess magnetic moments, have a significant effect on the formation of free radicals in the catalytic system itself.

Based on the published literature, phosphoromolybdic and tungsten phosphoric acids forming polyoxometallate clusters were preliminarily tested to select an effective liquid-phase epoxidation catalyst for styrene and  $\alpha$ -methylstyrene. In the course of the work, various REE-containing samples of polyoxometallates were prepared and their activity in the above reaction was checked. To increase the selectivity for oxidation products and reduce the degree of styrene polymerization, an n-butanol solution of boric acid (3.0 wt%  $H_3BO_3$  in butan-1-ol) and an  $\alpha$ -naphthol polymerization inhibitor were used in the experiments. In order to determine the dependence of the efficiency of the synthesized catalytic systems of polyoxomolybdate and polyoxungstate modified by rare-earth metal compounds in the

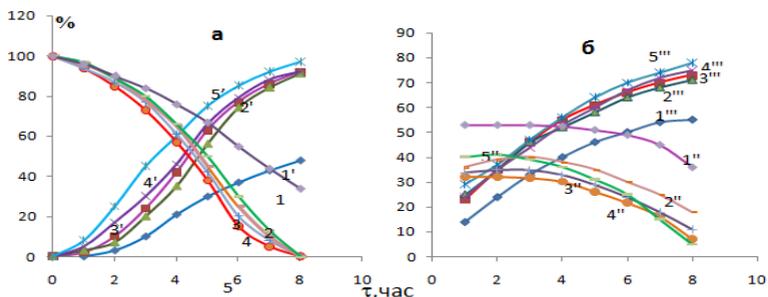
oxidation of unsaturated hydrocarbons with hydrogen peroxide, physicochemical studies were carried out using IR, NMR spectroscopy, EPR, electron microscope, and X-ray phase analysis. The experimental results [6, 7, 8, 10, 12-19, 22] showed that the conversion of styrene and the yields of hydroxy products, depending on the nature of REE modifiers, polyoxometallate and the source of an active oxygen, vary over a wide range.

### **3. The influence of various factors on the conversion and direction of conversion of styrene**

Studies have shown that the composition of the oxidate substantially depends on the concentration and quantity of the selected oxidizing agent. Taking into account this, the effect of the concentration of the oxidizing agent and the molar ratio of substrate: oxidizing agent were studied on the selected catalyst of the composition  $\text{CePO}_4 \cdot \text{PW}_{12}\text{O}_{41} \cdot n\text{H}_2\text{O}$  on the mesoporous carbon material [12-19].

Styrene was oxidized in two versions: a) an aqueous solution of  $\text{H}_2\text{O}_2$  and b) an adduct of  $\text{H}_2\text{O}_2$  with  $\text{CO}(\text{NH}_2)_2$  (hydroperite). The primary oxidation product is phenyloxirane. However, regardless of the oxidizing agent selected, the oxidate contains benzaldehyde, phenylacetaldehyde, phenylethan-1,2-diol or its monoacetate and benzoic acid. Their ratio depends on the concentration of the oxidizing agent and the temperature. With a minimum ratio of St:  $\text{H}_2\text{O}_2 = 1:0.5-1$  and a temperature not exceeding  $70\text{ }^\circ\text{C}$ , the yield of epoxide on the converted substrate is 26.4-47.6%. When using an acetic acid solution of hydroperite (an adduct of  $\text{H}_2\text{O}_2$  and urea) as an oxidizing agent, the composition of the oxidate is significantly different. Under the same conditions, the main reaction products are phenyloxirane and phenylethan-1,2-diol monoacetate. With an increasing the molar ratio of St:  $\text{H}_2\text{O}_2$  from 1: 0.5 to 1: 2, the induction period of styrene oxidation decreases. Probably, an excess of hydrogen peroxide is involved in the formation of the corresponding peroxocomplex from polyoxotungstate, which is

involved in the transfer of active oxygen  $H_2O_2$  to the substrate molecule(pic.1).



**Figure 1. Dynamics of conversion of styrene and hydrogen peroxide (a) and accumulation of styrene oxidation products (b) depending on the mole ratio  $St:H_2O_2$ . The catalyst  $CePO_4 \cdot PW_{12}O_{41} \cdot n H_2O / MCM$   $T=70^\circ C$ . Molar ratio  $St:H_2O_2$ - 1,1',1'',1'''-1:0,5;2,2',2'',2'''-1:1;3,3',3'',3'''-1:1,2;4,4',4'',4'''-1:1,5;5,5',5'',5'''-1:2**

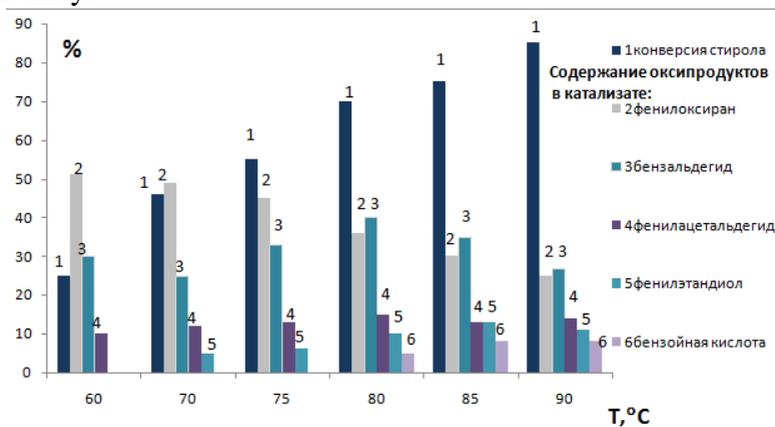
1-5- degree of conversion of  $H_2O_2$ ;1'-5'- the degree of conversion of styrene; 1''-5''- the yield of epoxide;1'''-5'''- output aldehydes

The temperature regime of the reaction has a significant effect on the conversion of styrene (Fig. 2). At a temperature of  $50^\circ C$ , styrene oxidation with an aqueous solution of  $H_2O_2$  proceeds with a long induction period. The yield of oxidation products at this temperature for 5 hours does not exceed 5-7%. However, the conversion of hydrogen peroxide reaches 48-52%. Probably, under these conditions, the transfer of active oxygen by the formed tungsten peroxo complex does not occur. Monomolecular decomposition of this complex occurs with the release of molecular oxygen. With an increase in temperature in the range of  $50-100^\circ C$ , the conversion of styrene sharply increases and reaches 92.0-98.0%. In this case, the content of phenyloxirane in the catalysis under other identical conditions ( $\tau = 7$  hours, the molar ratio of Styrene:  $H_2O_2 = 1: 2$ ) decreases from 52.5 to 26.0%, while the content of aldehydes and ketones (phenylacetic aldehyde, benzaldehyde, and phenylacetophenone) increases sharply.

The rate and composition of styrene oxidation products are also significantly affected by the nature of the solvents used and the rate of stirring of the reaction mixture.

When an aqueous solution of  $H_2O_2$  is used, the process proceeds under conditions of interphase catalysis - the tungsten peroxy complex is formed in an aqueous solution, and the oxidation of the substrate occurs in the interphase space and in the organic phase. The conversion of styrene increases with an increase in the stirring speed from 100 to 700 rpm. A further increase in the stirring rate of the solution from 700 to 1000 rpm has practically no effect on the conversion of the substrate. Taking into account the data obtained, the stirring rate in the oxidation reaction was maintained within the range of 600-700 rpm.

Both individual compounds and binary mixtures were used as a solvent. The highest conversion of styrene (62.6%) is achieved when using a binary mixture of solvents-toluene and dichloromethane at a ratio of 1: 1, while the oxidate composition does not change significantly.



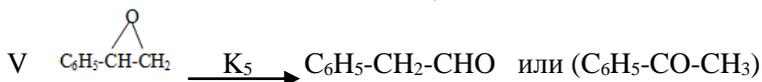
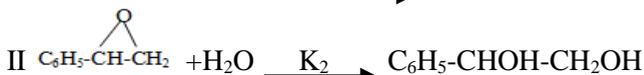
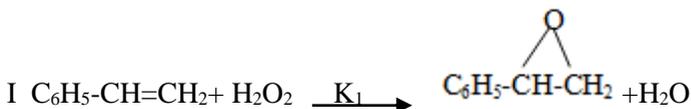
**Fig 2. Influence of temperature on styrene oxidation by 35% aqueous solution of  $H_2O_2$  and on the composition of the resulting oxidate ( $\tau = 7$  hours, molar ratio St:  $H_2O_2 = 1: 2$ ) in the presence of a catalyst  $CePO_4 \cdot PW_{12}O_{41} \cdot n H_2O$**

Based on the data obtained, the mixing rate in the oxidation reaction was maintained in the range of 600-700 rpm.

#### 4. Study of the kinetics and mechanism of styrene oxidation by hydrogen peroxide in the presence of the $\text{CePO}_4 \cdot \text{PW}_{12}\text{O}_{41} \cdot n\text{H}_2\text{O}$ catalyst system

The kinetic regularities and the mechanism of liquid-phase oxidation of styrene with hydrogen peroxide in the presence of polyoxotungstate modified with cerium cations have been studied [19].

Kinetic equations and a step-by-step kinetic model describing the main routes of the reaction are compiled. A set of the following independent routes of the oxidative conversion of styrene and the accumulation of reaction products is assumed:



The closest convergence of the calculated and experimental data is achieved by using the following kinetic equations of the power type:

$$r_1 = k_1 [c_1] [c_2] \quad (1)$$

$$r_2 = k_2 [c_3] \quad (2)$$

$$r_3 = k_3 [c_1] [c_2]^2 \quad (3)$$

$$r_5 = k_5 [c_3] \quad (5)$$

$$r_6 = k_6 [c_2] [c_4] \quad (6)$$

$$r_7 = k_7 [c_2] [c_6] \quad (7)$$

$$r_4 = k_4 [c_6] \quad (4) \qquad r_8 = k_8 [c_1] [c_2] \quad (8)$$

where  $k_1$ - $k_8$  are the reaction rate constants along routes I-VIII,  $r_1 - r_8$  is the rate of accumulation of reaction products according to the corresponding stoichiometric equations,  $C_1$ - $C_6$  is the concentration of compounds, mol/l. The rate of conversion of styrene and oxidation products obtained by routes I-VIII is calculated using the following equations:

$$\omega_1 = -r_1 - r_3 - r_8 \quad (9) \qquad \omega_4 = r_3 - r_6 + r_7 \quad (12)$$

$$\omega_2 = -r_1 - 2r_3 - r_6 - r_7 \quad (10) \qquad \omega_5 = r_4 + r_5 \quad (13)$$

$$\omega_3 = r_1 - r_2 - r_5 \quad (11) \qquad \omega_6 = r_2 - r_4 - r_7 \quad (14)$$

$$\omega_7 = r_6 \quad (15)$$

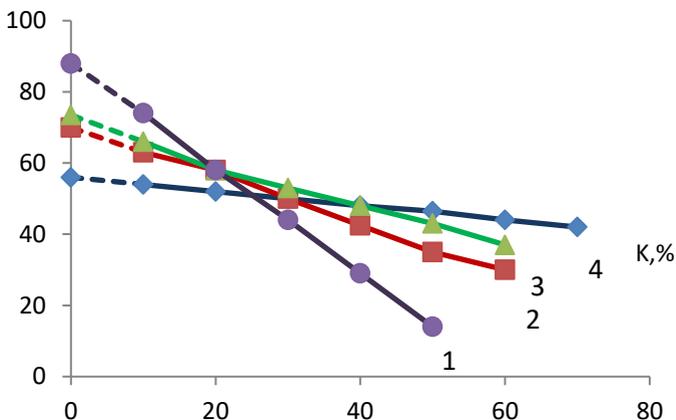
$$\omega_8 = r_8 \quad (16)$$

where  $\omega_1$ ,  $\omega_2$  - experimentally determined rates of consumption of styrene and active oxygen of hydrogen peroxide,  $\omega_3$ - $\omega_7$  - rates of accumulation of phenyloxirane, benzaldehyde, phenylacetaldehyde, phenylethane-1,2-diol, benzoic acid and the product of oxidative oligomerization.

It is assumed that the reaction proceeds according to a sequential scheme, by further conversion of the resulting epoxides. In order for testing this version, conversion curves for the conversion of styrene were constructed (Fig. 3.)

In coordinates  $S \rightarrow K$  ( $S$  is the selectivity for epoxide,  $K$  is the conversion of styrene). As can be seen from it, epoxy at  $K \rightarrow 0$  is not the only product of styrene oxidation (found by extrapolating the curves at different temperatures). Along with epoxide, phenylacetaldehyde, benzaldehyde, and phenylethane-1,2-diol are also formed. These results show that in this case the reaction proceeds through a parallel - sequential scheme for the conversion of styrene and oxidation products. This scheme is probably due to the formation of tungsten peroxo complexes with different structures that differ in their activity in this reaction. Probably, the formation of such styrene oxidation products as benzaldehyde, phenylacetaldehyde, and phenylethane-1,2-diol only through the stages of intermediate formation of epoxide can be considered

unreasonable. These reaction products can also be formed directly by oxidation of styrene itself along the above routes.



**Figure 3. Dependence the selectivity of the reaction for phenyloxirane on the conversion of styrene at different temperatures: 1. 50 °C 2. 70 °C, 3. 75 °C, 4. 80 °C**

To calculate the rate constants was used modified method fourth-order Runge-Kutta with applying for the Matlab-6.5 program. The experimental values of the constants were determined graphically using the method of initial velocities and were refined by minimizing the standard deviations between the observed and calculated data for equations (9) - (16).

With the found values of the constants for routes I-VIII in the case of using an aqueous solution of H<sub>2</sub>O<sub>2</sub>:

$$k_1 = 7 \cdot 10^6 \exp(-53649/RT) \text{ l} \cdot \text{mole}^{-1} \cdot \text{h}^{-1}$$

$$k_2 = 5 \cdot 10^6 \exp(-37579/RT) \text{ h}^{-1}$$

$$k_3 = 1.2 \cdot 10^8 \exp(-52731/RT) \text{ l} \cdot \text{mole}^{-1} \cdot \text{h}^{-1}$$

$$k_4 = 4 \cdot 10^6 \exp(-36859/RT) \text{ h}^{-1}$$

$$k_5 = 4.41 \cdot 10^5 \exp(-29846/RT) \text{ h}^{-1}$$

$$k_6 = 2 \cdot 10^6 \exp(-33337/RT) \text{ l} \cdot \text{mole}^{-1} \cdot \text{h}^{-1}$$

$$k_7 = 0.43 \cdot 10^2 \exp(-13034/RT) \text{ l} \cdot \text{mole}^{-1} \cdot \text{h}^{-1}$$

$$k_8 \approx 0$$

and in the case of using hydroperite:

$$k_1 = 2.1 \cdot 10^6 \exp(-48286/RT) \text{ l} \cdot \text{mole}^{-1} \cdot \text{h}^{-1}$$

$$k_2=6.1 \cdot 10^{11} \exp(-16885/RT) \text{ h}^{-1}$$

$$k_3=7.2 \cdot 10^{10} \exp(-15239/RT) \text{ l} \cdot \text{mole}^{-1} \cdot \text{h}^{-1}$$

$$k_4=2.1 \cdot 10^{10} \exp(-18784/RT) \text{ h}^{-1}$$

$$k_5=5.3 \cdot 10^{10} \exp(-23669/RT) \text{ h}^{-1}$$

$$k_6=6.2 \cdot 10^{10} \exp(-23669/RT) \text{ l} \cdot \text{mole}^{-1} \cdot \text{h}^{-1}$$

$$k_7=2.1 \cdot 10^4 \exp(-25314/RT) \text{ l} \cdot \text{mole}^{-1} \cdot \text{h}^{-1}$$

$$k_8 \approx 0$$

(R- universal gas constant  $8.3144 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ )

the best description of the reaction rate of liquid-phase styrene oxidation is obtained. The standard deviation calculated by equations (9) - (16) and experimental data for routes I-IV was 9.2-11.4%, and for routes V-VII 14.6-18.0%. A zero  $K_8$  value indicates that the main routes of styrene conversion are its oxidation to aldehydes and oxirane via routes (I) - (VII). Other types of equations lead to worse agreement and in all cases turned out to be less correct.

Based on the results obtained, a kinetic model of the styrene epoxidation process was compiled, which can be used in mathematical modeling.

## **5. Epoxidation and oxidative conversion of C<sub>9</sub>, C<sub>12</sub> macrocyclic unsaturated hydrocarbons and pyrocondensate with the participation of hydrogen peroxide and cerium polyoxotungstate**

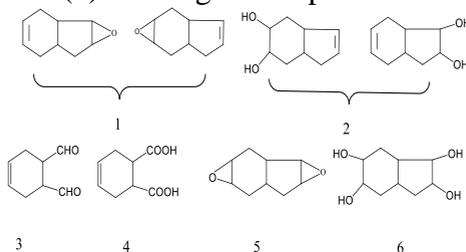
According to the literature and our studies, pyrolysis product isolated from liquid pyrolysis products contains other unsaturated hydrocarbons along with styrene and its methyl derivatives. In particular, the fraction 130-190 °C contains a significant amount of indene and cyclopentadiene dimer. The liquid phase oxidation of these hydrocarbons with hydrogen peroxide proceeds according to a complex scheme, with the formation of various oxidation products, including epoxides, aldehydes, and polyols.

In contradistinction to styrene and its methyl derivatives in the tetrahydroindene molecule (bicyclo [4.3.0] nona-3.7-diene), along with two multiple bonds, there are also two tertiary carbon atoms that are easily attacked by active oxygen. That is, the oxidation product of

bicyclo-[4.3.0]none-3.7-diene should be rather complex [1, 2, 9, 20, 21].

We studied the influence of various factors, which showed that the conversion of the initial hydrocarbon and the composition of the obtained oxidate significantly depends on such factors as the concentration of acids and hydrogen peroxide, temperature, duration of the experiment, the amount of catalyst and the molar ratio of substrate: oxidizing agent.

According to GLC, chromatography-mass and IR spectroscopy, as well as chemical analysis methods, we detected in the products of tetrahydroindene oxidation monoepoxide (1), diol (2), dialdehyde (3), dibasic acid (4) under more severe conditions, diperoxide (5) tetraol (6) and oligomeric products.



Considering the above liquid-phase oxidation of tetrahydroindene with the participation of hydrogen peroxide in the presence of cerium-containing peroxotungstate was carried out under the conditions of a shallow conversion of the initial hydrocarbon.

In the studied region, the oxidation of THI, unlike styrene and its methyl derivatives, mainly proceeds in the direction of epoxidation and dihydroxylation. The formation of products of deeper oxidation of  $\alpha$ -polyols, aldehydes, and acids is observed under severe conditions. So, if in the presence of acetic acid at a molar ratio of THI:  $\text{CH}_3\text{COOH}$ :  $\text{H}_2\text{O}_2 = 1:0.2:2$  at a temperature of  $70^\circ\text{C}$  and a duration of 3 hours, with a conversion of THI of 31.7%, the selectivity for monoepoxide is 20.5%, then an increase in the duration of the experiment to 7 hours leads to a decrease in its amount in the oxidate to 14.5%. A decrease in its amount is due to

hydrolysis, which leads to an increase in the diol content in the catalyst. Moreover, both in the case of epoxidation and dihydroxylation (Table 1), the reaction mainly proceeds via multiple bonds of the five-membered THI cycle. According to the data of NMR<sup>1</sup>H and <sup>13</sup>C analysis, the intensity of signals from protons of the multiple bond of the cyclopentene fragment of THI (in NMR<sup>1</sup>H  $\delta=5.26-5.41$  ppm) after oxidation is greatly reduced. The signals of the -CH=CH- cyclohexene fragment protons ( $\delta=5.78-5.96$  ppm) practically remain unchanged. Moreover, the signals from the epoxy cycle protons ( $\delta=3,75-3,95$  ppm) correspond to the epoxy fragment of methylepoxycyclopentane.

**Table.1**

**The effect of the concentration of acetic acid and hydrogen peroxide on the composition of the products of the oxidation of tetrahydroindene with an aqueous solution of hydrogen peroxide (catalyst CePO<sub>4</sub> ·PW<sub>12</sub>O<sub>41</sub>·n H<sub>2</sub>O/MCM-15g/l, T=70°C,  $\tau=7$ h, molar ratio THI: H<sub>2</sub>O<sub>2</sub>=1:2, C<sub>THI</sub>=0,05 mole**

Concentration of CH <sub>3</sub> COOH, %	Concentration of H <sub>2</sub> O <sub>2</sub> , %	Conversion THI, %	The composition of oxidate, mole%					
			mono-epoxide	diol	glycol monoacetate	$\alpha$ -oxyketone	diepoxide	Returned THI
95	35	76,4	14,5	50,8	9,4	3,0	2,8	19,5
80	35	75,3	12,8	53,5	9,6	1,9	1,9	20,3
65	35	66,0	10,5	56,9	1,8	-	-	30,8
50	35	41,3	10,5	30,3	6,6	-	-	52,6
30	35	22,4	7,2	19,5	-	-	-	73,3
95	28	71,0	12,7	51,7	6,8	-	4,6	24,2
95	23	54,8	11,2	44,6	4,9	-	-	39,3
95	18	20,3	5,4	18,7	-	-	-	75,9

\* jointly with glycol monoacetate

According to GLC analysis of the fraction 85-87 °C/0.5 kPa consists of two isomers, with a mass ratio of a: c= 87: 13 [3-

oxatricyclo[4.4.0<sup>1.6</sup>.0<sup>2.4</sup>]dec-8-ene (a): 4 -oxatricyclo [5.3.0<sup>1.7</sup>.0<sup>3.5</sup>]dec-8-en (c)]. This fraction has the following characteristics:

T. boil. 85-87 °C / 0.5 kPa;  $n_D^{20}$  1.5154,  $d_4^{20}$  0.9842. According to the IR spectrum,  $\nu$ , cm<sup>-1</sup>: 3020 ( $\nu_1$ = CH), 2935 ( $\nu_1$ , CH<sub>2</sub>), 1640 ( $\nu$ , C = C), 1240, 1200, 920, 840 (oxirane fragment) NMR <sup>1</sup>H-spectrum,  $\delta$ , ppm: 5.78-5.96 (2H, 2CH = cyclohexane fragment), 5.26-5.41 m (2H, 2CH = cyclopentane fragment) 3.75-3.90 m (protons of CH, oxirane fragment) 1.60-2.45 m (protons of CH and CH<sub>2</sub> of the five- and six-membered ring).

A mixture of bicyclo [4.3.0<sup>1.6</sup>]non-7-en-3,4-diol and bicyclo [4.3.0<sup>1.6</sup>] non-3-en-7,8-diol is characterized by the following IR spectrum data 3411-3398( $\nu$ ,OH), 3050-3040( $\nu$ ,=CH),1640( $\nu$ ,C=C), 1340,1380( $\delta$ ,CH),110-1078( $\delta$ ,OH). NMR <sup>1</sup>H,  $\delta$ , ppm:6.15m (1H CH<sup>7</sup>=), 6.41 m (1H, CH<sup>8</sup>=), 4,8 C(OH), 1,48-2.28 m (6H,3CH<sub>2</sub>).

**Table 2.**  
**Liquid-phase oxidation of tetrahydroindene with a 35% aqueous solution of H<sub>2</sub>O<sub>2</sub> in the presence of CePO<sub>4</sub>·PW<sub>12</sub>O<sub>41</sub>·nH<sub>2</sub>O/MCM, cetyltrimethyl ammonium bromide (phase transfer agent), and triethyl ammonium dihydrogen phosphate (ionic liquid). (molar ratio THI H<sub>2</sub>O<sub>2</sub>:CTMB:IL=100:200:1:1, T=70°C, C<sub>CH<sub>3</sub>COOH</sub>=0,01 mole,C<sub>THI</sub>=0,05 mole):**

$\tau$ ,h	Conversion of THI, %	The composition of oxidate, mole%					Yield, %	
		Mono-epoxide	diol	glycol monoacetat	diepoxide	Unsaturate <sub>d</sub>	Epoxide	diol*
1	18,4	67,0	28,2	4,8	-	-	12,3	6,1
2	31,2	54,5	36,6	5,2	2,0	1,7	17,0	13,0
3	40,4	47,3	42,1	4,8	2,0	3,8	19,1	18,9
4	52,3	36,8	49,4	5,7	3,0	5,1	19,2	28,8
5	61,8	26,2	57,0	6,0	3,2	7,6	16,2	38,9
6	71,0	18,3	65,0	4,3	3,8	7,4	13,0	49,2
7	79,2	17,2	72,4	3,7	2,9	5,0	13,6	60,3

\* jointly with glycol monoacetate

Taking into account the foregoing, the epoxidation and dihydroxylation of THI with hydrogen peroxide in the presence of  $CePO_4 \cdot PW_{12}O_{41} \cdot nH_2O/MCM$  was carried out with the participation of cetyltrimethylammonium bromide (CTMB) (phase transfer agent) and triethylammonium dihydrogen phosphate. The results of the studies are shown in table.2.

In contrast to the supported catalyst, when using non-supported  $CePO_4 \cdot PW_{12}O_{41} \cdot nH_2O$  CTMB and triethylammonium dihydrogen phosphate at 70 °C and a duration of 4 hours, the conversion of THI and the composition of the oxidate change significantly (Table 3). Under these conditions, the THI conversion is 57.4, and the epoxide yield is 28.2%. In this case, the diol yield remains almost unchanged. However, with increasing duration of up to 7 hours, the yield of diol also increases and reaches 60.2%.

**Table 3.**  
**Liquid-phase oxidation of tetrahydroindene with a 35% aqueous solution of H<sub>2</sub>O<sub>2</sub> in the presence of CePO<sub>4</sub>·PW<sub>12</sub>O<sub>41</sub>·nH<sub>2</sub>O, cetyltrimethylammonium bromide (phase transfer agent) and triethylammonium dihydrogen phosphate (ionic liquid) (molar ratio THI:H<sub>2</sub>O<sub>2</sub>:CTMB: IL=100:200:1:1, T=70°C, C<sub>CH<sub>3</sub>COOH</sub>=0,01 mole, C<sub>THI</sub>=0,05 mole)**

τ, h	Conversion of THI, %	The composition of oxidate, mole%					Yield, %	
		Mono-epoxide	diol	glycol monoacetat	diepoxide	Unsaturated compounds	epoxide	diol
1	23,0	71,4	24,7	3,9	-	-	16,4	6,6
2	34,7	70,3	26,0	2,2	1,5	-	24,4	9,8
3	48,3	57,6	32,2	4,1	2,8	3,3	27,8	17,5
4	57,4	49,2	42,1	4,1	2,1	2,5	28,2	26,5
5	65,2	35,0	53,6	5,2	3,6	2,6	22,8	38,3
6	76,0	27,0	62,4	5,1	3,4	2,1	16,8	51,3
7	83,8	25,2	67,0	4,8	0,8	2,2	21,1	60,2

It is likely that when using homogeneous cerium polyoxytungstate, the peroxocomplex formed in the aqueous phase is transferred with the aid of CTMB to the organic phase and actively participates in the reactions of epoxidation and dihydroxylation of THI molecules.

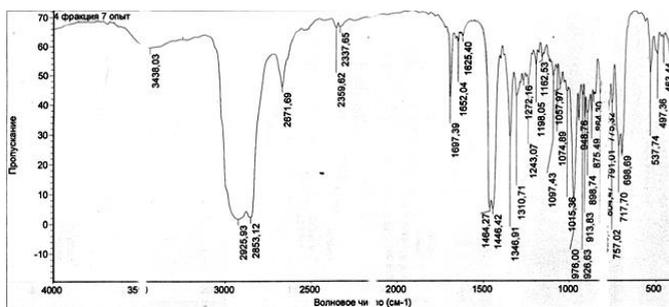
## **6. Epoxidation and dihydroxylation of cyclododecene with hydrogen peroxide in the presence of cerium polyoxophosphoric tungstate**

This section presents the results of epoxidation of cyclododecene (CDD) with hydrogen peroxide in the presence of  $\text{CePO}_4 \cdot \text{PW}_{12}\text{O}_{41} \cdot n\text{H}_2\text{O}$  / MCM [5, 11, 23].

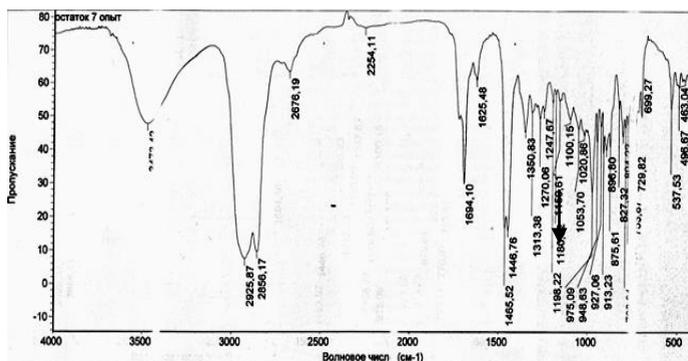
Oxidation of this macrocyclic hydrocarbon was carried out under the conditions previously found for THI.

The study was carried out in a thermostated glass microreactor equipped with a thermometer, a dropping funnel and a refrigerator, with vigorous stirring of the reaction mixture (700 rpm) with a magnetic stirrer. The calculated amount of cyclododecene, toluene as a solvent and catalyst, and acetic acid was simultaneously added into the reactor to achieve the required pH value. After reaching the required temperature (50-100 ° C) with vigorous stirring, a 35% aqueous solution of  $\text{H}_2\text{O}_2$  or an acetic acid solution of hydroperite was added dropwise.

The analysis of the products carried out by the method of IR spectroscopy (Fig. 4) showed that the oxidation of cyclododecene proceeds mainly in the directions of epoxidation and dihydroxylation. To find the optimal conditions for the release of epoxy cyclododekane, the effect of temperature, duration of the experiment, the amount of catalyst, and the molar ratio of substrate: oxidant were studied.



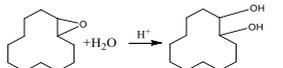
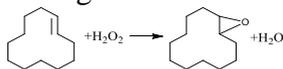
**a**



**b**

**Fig.4. IR spectra of cyclododecene oxidate: in the organic phase (a) after removal of the solvent; and the residue (b) isolated by extraction from the aqueous phase**

Direction of reaction along the routes:



depends on the acidity of the aqueous phase and the reaction temperature (Table 4.). As can be seen from the data in the table, the direction of the reaction along the above routes is determined by the pH value of the medium. At  $\text{pH} > 4$ , the activity of the catalytic system decreases significantly and the proportion of unproductive thermocatalytic decomposition of hydrogen peroxide increases.

**Table 4.**  
**Influence of a number of factors on the selectivity of**  
**formation epoxycyclododecene (13-oxabicyclo [10.1.10<sup>1,12</sup>]**  
**tridecane and cyclododecene-1,2-diol) upon oxidation of**  
**cyclododecene by 35% aqueous solution of H<sub>2</sub>O<sub>2</sub> (molar ratio**  
**CDD: H<sub>2</sub>O<sub>2</sub>:CH<sub>3</sub>COOH=1:2:0,2)**

T, °C	τ, h	pH- aqueous phase	amount of cat. g / l	conversion, %		selectivity, %	
				CDD	H <sub>2</sub> O <sub>2</sub>	By epoxide	By diol
50	7	2.5	15	42.3	79.4	89.7	10.3
60	7	2.5	15	44.0	81.8	88.8	11.2
70	7	2.5	15	57.2	89.0	82.2	17.8
80	7	2.5	15	69.8	95.0	57.4	42.6
90	7	2.5	15	77.2	96.1	50.2	49.8
70*	7	1.5	15	81.8	97.4	24.8	75.2
70*	7	1.8	15	80.4	92.3	26.5	73.5
70	7	2.0	15	79.6	94.8	31.1	68.9
70	7	3.0	15	68.0	91.7	70.4	29.6
70	7	4.0	15	64.2	89.6	78.3	21.7
70	3	3.0	15	44.6	58.2	73.0	27.0
70	5	3.0	15	58.4	69.0	75.2	24.8
70	8	3.0	15	74.0	94.9	69.0	31.0
70	7	3.0	10	67.5	76.3	49.0	51.0
70	7	3.0	5	54.5	68.2	44.7	55.3
70	7	3.0	20	74.7	92.0	71.7	29.3

\* in the presence of formic acid.

The formation of 13-oxabicyclo [10.1.10<sup>1,12</sup>]tridecane in a high yield (75.2-78.3%) per converted CDD is achieved at a temperature of 85-90 ° C, a duration of 6-7 hours and a pH of the aqueous phase of 2.5-3. A decrease in the pH value to 1.5-2 and an increase in temperature to 90-100 ° C leads to an increase in the yield of cyclododecene-1,2-diol (Table 4).

## **7. Liquid-phase oxidation of the 130-190 ° C fraction of pyro condensate with hydrogen peroxide in the presence of cerium-containing polyoxotungstate**

It is known that one of the main processes of modern petrochemistry is the purposeful processing of liquid pyrolysis products. In particular, on the basis of light and heavy fractions of pyrolysis condensate, industrial processes have been developed for obtaining high-octane components of gasoline, individual products - isoprene, cyclopentene, cyclopentadiene (or its dimer), styrene, etc. Processes such as hydrogenation purification and extractive distillation with the participation of N-methylpyrrolidone, dimethylacetamide are used.

During the hydrogenation purification of these fractions, diene hydrocarbons are converted into monoolefins, which form resinous compounds during the operation of gasoline.

It should be noted that the composition of individual fractions of pyrolysis condensate significantly depends on the feedstock of the pyrolysis process. Table 5 shows the composition of the 130-190 ° C fraction of pyrolysis condensate obtained from the pyrolysis of straight-run gasoline and the return hydrocarbon fraction after oxidation.

Unsaturated hydrocarbons in real conditions in the composition of diesel fuel under the action of structural materials enter into an oxidation reaction with oxygen dissolution in it, which leads to an increase in the amount of resins.

Considering that unsaturated hydrocarbons are easily subject to oxidation, we set the task of preliminary oxidation of individual fractions of pyrolysis condensate, bypassing the stage of separating unsaturated hydrocarbons from its composition and determining the practical usefulness of the obtained oxidate [3, 4, 20].

Inasmuch as, the fraction of 130-190 ° C of pyrocondensate contains unsaturated hydrocarbons, which are the subject of our research - (styrene and its methyl derivatives, indene, cyclopentadiene dimer) the content of which reaches 27-28%, for the subsequent research this fraction was chosen. As can be seen from

Table 5, the main unsaturated hydrocarbons of this fraction are: styrene 11.7,  $\alpha$ -methylstyrene 6.2, cyclopentadiene dimer 4.0, vinyl toluene isomers 3.2, indene 2.8.

**Table 5.**  
**The composition of the initial mixture fr. 130-190 °C**  
**pyrocondensate and the return of the hydrocarbon fraction after**  
**oxidation**

The composition of initial raw material	% wt	The composition of return hydrocarbon	% wt
benzene	3,0	Benzene	
toluene	12,6	toluene	4,0
ethylbenzene	4,6	ethylbenzene	16,8
xylene isomers	16,4	xylene isomers	6,1
styrene	11,7		21,9
trimethylbenzene isomers	9,0	trimethylbenzene isomers	
$\alpha$ -methylstyrene	6,2	$\alpha$ -methylstyrene	12,0
dicyclopentadiene	4,0	dicyclopentadiene	0,1
isomers of vinyl toluene	3,2	indan	0,4
indan	5,2	inden	6,9
inden	2,8		0,2
aromatic hydrocarbons	8,4	aromatic hydrocarbons	11,2
C <sub>10</sub>		C <sub>10</sub>	20,4
unidentified compounds	12,9	unidentified compounds	

Oxidation of this fraction was carried out in a thermostated glass reactor equipped with a thermometer, a dropping funnel, and a refrigerator with vigorous stirring of the reaction mixture (700 rpm). The calculated amount of fr 130-190 ° C, catalyst and acetic acid was simultaneously loaded into the reactor to achieve the required pH-value of the aqueous medium. After reaching the temperature of the reaction mixture of 90-100 ° C, a 35% aqueous solution of H<sub>2</sub>O<sub>2</sub> was added dropwise over 1 hour. Stirring of the reaction medium was

continued for 6-8 hours. The organic layer was separated from the aqueous. The aqueous layer was extracted twice with a mixture of toluene and 2-propanol. The extract and organic layer were combined and subjected to atmospheric distillation.

The composition of the initial and unreacted mixture is presented in Table 5. The iodine number of the return hydrocarbon mixture is 2.0.

The conversion of unsaturated hydrocarbons under the above conditions reaches 97.4%.

According to GLC and IR-analysis of the obtained oxidate, the main oxygen-containing products are oxiranes, monoacetates of the corresponding diols, and aromatic aldehydes.

The resulting oxygenate was tested as a smoke control additive for diesel fuel. It was found that the addition of oxygenate in an amount of 0.25-1.0 wt% contributes to a significant reduction in smoke when burning diesel fuel. The oxygenate test report is presented in the dissertation work.

## RESULTS

1. The method of liquid-phase oxidation of styrene,  $\alpha$ -methyl- and p-methylstyrenes to the corresponding aldehydes and epoxides in the presence of the pseudo-homogeneous catalyst system  $\text{CePO}_4 \cdot \text{PW}_{12}\text{O}_{41} \cdot n\text{H}_2\text{O}/\text{MCM}$ , prepared on the basis of ammonium dodecatungstate, cerium (III) nitrate,  $\text{H}_3\text{PO}_4$  and mesoporous carbon material was worked out for the first time [6-8, 23].

2. The influence of various factors (temperature, duration, the molar ratio of reagents, nature of the oxidizing agent and amount of catalyst) on the conversion of styrene, its methyl derivatives and the composition of the oxidate were studied. It was found out that the conversion of styrene and its methyl derivatives proceeds in two directions.

- epoxidation at multiple bonds without changing the structure of the original substrate.

-isomerization of the oxirane cycle with the formation of the corresponding aldehydes. With a styrene conversion of 25.0-44.3% phenyloxirane selectivity reaches 46.3-52.6%, and with a conversion of 68.7-96% the total selectivity for benzaldehyde and phenylacetaldehyde comprises 55-60%.

Under optimal conditions the conversion of  $\alpha$ -methylstyrene is 68.5-76.2%, and the selectivity for 2-phenylpropanal (hydratropic aldehyde) is 81.9-85.3% [12-19].

**3.** The kinetic laws and the mechanism of liquid-phase oxidation of styrene with hydrogen peroxide in the presence of  $\text{CePO}_4 \cdot \text{PW}_{12}\text{O}_{41} \cdot n\text{H}_2\text{O}/\text{MCM}$  were studied. Based on the totality of the obtained experimental and calculated data carried out using the modified fourth-order Runge-Kutta method and Matlab-6.5 program, a kinetic model of the process was compiled and the values of kinetic independent routes were calculated [19].

**4.** In the presence of a cerium phosphate-polyoxotungstate system, the catalytic oxidation of tetrahydroindene with hydrogen peroxide at a temperature of 50-80 °C was studied, and it was found out that unlike styrene and its methyl derivatives, the main reaction products are the corresponding monoepoxides and diols. When using hydroperite at 50-60 °C and continuing the experiment for 3-4 hours, the conversion of THI is 62.4-65.7%, and the yield of mono epoxides 72-75.5% for converted THI. It was established that THI mono epoxide consists of two isomers: 3-oxatricyclo- [4.4.0<sup>1.6</sup>.0<sup>2.4</sup>] and 4-oxatricyclo [5.3.0<sup>1.7</sup> 0<sup>3.5</sup>] dec-8-ene with a molar ratio 4:1. With an increasing the temperature from 60 to 80 °C and a duration of up to 8 hours, the amount of mono epoxides decreases, but the amount of diols increases [9, 20, 21].

**5.** The catalytic oxidation of macrocyclic unsaturated hydrocarbon cyclododecane with hydrogen peroxide to the corresponding mono epoxide was studied for the first time. The maximum yield of 13-oxabicyclo [10.1.0 1<sup>12</sup>] tridecane of 75.2-78.3% for the embellished CDD is achieved at a temperature of 85-90 °C and lasts 6-7 hours and for the pH of the aqueous phase lasts 2.5-3 hours. A decrease in pH to 1.5-2 and an increase of temperature

to 90-100 ° C lead to an increase in the yield of cyclododecane-1,2-diol from 21.7 to 75.2% [5, 11, 23].

**6.** The process of catalytic oxidation of a fr. 130-190 ° C of pyrocondensate (containing unsaturated hydrocarbons 27.9%) by hydrogen peroxide was studied and the conditions for the production of oxygenate of a certain composition were established. The oxygenate fraction isolated from the obtained catalysis was tested as an anti-smoke additive to diesel fuel. It is established that the addition of the obtained oxygenate in an amount of 0.25-1.0% to diesel fuel significantly reduces its smoke during use [3, 4, 20].

**MAIN CONTENT OF DISSERTATION IS STATED IN  
THE FOLLOWING  
PUBLICATIONS:**

1. Garibov, N.İ., Alimardanov, H.M., Musayeva, E.S. Heteropoly compounds of tungsten and molybdenum modified containing rare-earth elements as active catalysts of oxydation unsaturated alicyclic C<sub>6</sub>-C<sub>12</sub> hydrocarbons in the presence of hydrogen dioxide // X International Conference "Mechanisms of Catalytic Reactions",- Svetlogorsk, Kaliningrad Region, Russia:- October 2-6,- 2016,- p. 206
2. Alimardanov, H.M., Dadashova, N.R., Almardanova, M.B., Musaeva, E.S. Epoxidation of tetracyclo [6.2.1.1<sup>3.602.7</sup>] dodec-4-ene and its alkyl derivatives with hydrogen peroxide in the presence of polyoxoperoxometallate catalysts. // Chemical reagents, reagents and small-scale chemistry processes Reagent-2016. XXX International scientific and technical conference dedicated to the memory of academician of the Republic of Belarus Dilyus Lutfullich Rakhmankulov, - Ufa: - 14-16 november, -2016,- p. 39-40
3. Alimardanov H.M., Garibov N.I., Musaeva.E.S. Liquid-phase oxidation of the pyro-condensate fraction 120-150°C with hydrogen peroxide with the participation of GPS modified cations of cerium and gadolinium / IX Baku International Mamedaliyev Conference on Petrochemistry October 4 - 5, 2016, p. 79
4. Dadashova, N.R., Rzaeva, N.A., Djafarova, R.A., Garibov, N.I., Alimardanov, H.M., Musaeva, E.S. Liquid-phase oxidation of C<sub>7</sub>-C<sub>9</sub>-cycloolefins with hydrogen peroxide with the participation of REE-containing polyoxomolybdenum systems // IX Baku International Mamedaliyev Conference on Petrochemistry,- Baku: 4 – 5 October,- 2016,- p. 80
5. Alimardanov, H.M., Garibov, N.I., Musaeva, E.S., Huseynova, M.E., Kuliev, A.D. Epoxidation of cyclododecene with hydrogen peroxide in the presence of REE-containing heteropolysilanes // Proceedings of the International Annual

Scientific-Practical Conference "Actual Problems of Modern Chemistry and Biology" Dedicated to the 93rd Anniversary of the birth of the National Leader Heydar Aliyev, -Baku: -12-13 May, v. I, -p.124-128

6. Alimardanov, H.M., Garibov, N.I., Musaeva, E.S. Tungsten and molybdenum heteropoly compounds modified by rare-earth metal cations, as active catalysts for the oxidation of C<sub>6</sub>-C<sub>12</sub> unsaturated alicyclic hydrocarbons with hydrogen peroxide // IV International Scientific Conference Of Young Researchers 1 St Book, -Baku: - 2016, - p.237-238

7. Alimardanov, Kh.M, Garibov, N.I., Djafarova, R.A., Dadashova, N.R., Musayeva, E.S. Polyoxocomplexes containing rare earth elements (Gd, Nd, Ce, La) as effective catalysts of oxidation reaction of unsaturated hydrocarbons in the presence of hydrogen peroxide // International scientific and technical conference "Petrochemical synthesis and catalysis in complex condensed systems", dedicated to the 100th anniversary of Academician B.K. Zeynalov, - Baku: - 29-30June, - 2017, - p.157

8. Alimardanov, H.M., Garibov, N.I., Najafova, M.A., Kasumov, R.J., Musaeva, E.S. Influence of the nature of modifying additives of REE oxides on the properties of molybdenum and tungsten-containing heteropoly compounds / II Russian Congress on Catalysis "ROSKATALIZ"- Nizhny Novgorod, Novosebirsk:- 22-26 may, -2017,- p.621

9. Alimardanov, Kh.M., Sadigov, O.A, Garibov, N.I., Dadashova, N.R., Almardanova M.B. Epoxidation of tetracyclodecene hydrocarbons H<sub>2</sub>O<sub>2</sub>•CO (NH<sub>2</sub>)<sub>2</sub> in the presence of heteropolyside compounds containing rare-earth metal cations // Russian journal of general chemistry,- Saint Petersburg:- 2017.-v. 87,- Issue 2, -p.208-214

10. Alimardanov, H.M., Garibov, N.I., Najafova, M.A., Musaeva, E.S. Radical nature of terbium-polyoxy-tungsten systems in the presence of H<sub>3</sub>PO<sub>4</sub> and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> acids // International scientific and technical conference "Petrochemical synthesis and catalysis in

complex condensed systems" dedicated to the 100th anniversary of academician B.K. Zeynalov, Baku: - 29-30 June,- 2017,- p.184

**11.** Alimardanov, H.M., Garibov, N.I., Najafova, M.A., Musaeva, E.S. Praseodymium polyoxotungstate as a catalyst for the epoxidation of dodecene with hydrogen peroxide / Republican Scientific Conference dedicated to the 110th anniversary of Academician Murtuz Nagiyev, Baku: -2018, - p. 205

**12.** Alimardanov, H.M., Garibov, N.I., Najafova, M.A., Musaeva, E.S. Epoxidation of styrene with hydrogen peroxide in the presence of Tb- and Pr-containing polyoxytungstates / Proceedings of the International Annual Scientific and Practical Conference "Actual Problems of the Contemporary Chemistry And Biology" Dedicated to the 95th Birthday of National Leader Heydar Aliyev, Baku:- 04-05 may,-2018, -p. 325-328

**13.** Alimardanov, H.M. Study of the radical nature of terbium polyoxytungstate, a styrene epoxidation catalyst / H.M. Alimardanov, N.I. Garibov, M. A. Najafova, E.S. Musaeva // - Moscow: Oil Refining and Petrochemicals, - 2018, - № 4, -p. 25-30

**14.** Garibov, N.I., Alimardanov H.M., Najafova, M.A., Musayeva.E.S. Epoxidation of styrene with hydrogen peroxide in the presence of Tb- and Pr-containing polyoxotungstates // XII International Conference of Young Scientists on Petrochemistry,- Zvenigorod:- 04-05 may,-2018,- p.435-439

**15.** Alimardanov, H.M., Garibov, N.I., Musaeva, E.S. Epoxidation of styrene with hydrogen peroxide in the presence of REE-containing heteropoly compounds / International Scientific and Practical Conference dedicated to the 110th anniversary of Academician V.S.Aliyev "Innovative prospects for the development of oil refining and petrochemicals", Baku:- 9 – 10 october, -2018, - p.63

**16.** Alimardanov, H.M., Garibov, N.I., Najafova, M.A., Musaeva, E. S. Tb- and Pr-containing polyoxy-tungstates as catalysts for the epoxidation of styrene with hydrogen peroxide // «World of

Petroleum Products. Bulletin of Petroleum Companies», Moscow: - 2019, -p. 9-23

**17.** Musaev.E.S. Oxidation of  $\alpha$ -methylstyrene with hydrogen peroxide in the presence of cerium-containing polyoxalophromate. //Kazan: Young Scientist,-2019, -№49 (287), p. 11-17

**18.** Alimardanov, H.M., Garibov, N.I., Najafova, M.A., Musaeva, E.S., Dadashova, N.R. Liquid-phase oxidation of styrene and its methyl derivatives in the presence of REE-containing tungsten-phosphorus catalysts // International scientific conference "Actual problems of modern chemistry ", dedicated to the 90th anniversary of the Institute of Petrochemical Processes named after Academician Yu.G. Mamedaliev, Baku:-2-4 october,-2019,- p.368-369

**19.** Alimardanov, Kh.M., Velieva, F.M., Garibov, N.I., Musaeva, E.S. Kinetic laws of liquid-phase oxidation of styrene with hydrogen peroxide in the presence of polyoxotungstate modified with cerium cations. //- Saint Petersburg: Journal of Applied Chemistry,- 2020, - v. 93 , issue 5 ,p.722-734

**20.** Musaev, E.S. Catalytic liquid-phase oxidation of the 130-190 °C fraction of pyrocondensate with hydrogen peroxide with the participation of cerium-containing polyoxotungstate //Sumgait: SCIENTIFIC NEWS,- 2020,- v. 20, -№3,- p. 29-31

**21.** Musaeva, E.S. Oxidation of tetrahydroindene with hydrogen peroxide in the presence of cerium-polyoxotungstate //-Baku: Petrochemical and petroleum refining processes,- 2020, -v. 20, -№3, -p.362-371

**22.** Musayeva, E. S. Oxidation of n-methyl styrene (n-vinyltoluene) with hydrogen peroxide in the presence of cerium-containing samples of polyoxotungstate // USA, -New York: American Scientific Journal, -2020, -№ (35), -p. 41-45

**23.** Alimardanov, Kh.M., Method of obtaining cycloolefins epoxide. Invention İ20200028, Republic Of Azerbaijan. Alimardanov, H.M., Garibov, N.I., Sadigov, O.A, Abbasov M.F., Musaeva, E.S., Almardanova M.B. Recorded in the state register: 15.07.2020

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