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RESEARCH ARTICLE OPEN ACCESS

Kinetics and Mechanism of the Reaction of Coherently Synchronized Oxidation and Dehydrogenation of Cyclohexane by Hydrogen Peroxide

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ABSTRACT
Inducing effect of hydrogen peroxide on synchronous oxidation reaction is accompanied by the occurrence of two interconnected and interacting reactions. The reaction of H_2O_2 decomposition (primary) generates the leading active $^{\bullet}OH$ and $HO_2^{\bullet}$ free radicals in a system. During the interaction of active and free radicals with the substrate, the conversion of the substrate occurs in the secondary reaction, coherently-synchronized with the primary one.

The mechanism of such coherently synchronized reactions is being examined in the process of cyclohexane oxidation with hydrogen peroxide in homogeneous and heterogeneous systems.

The process of coupling dehydrogenation of cyclohexane to cyclohexene and cyclohexadiene with hydrogen peroxide was carried out without catalyst. This process was also carried out at a fairly low temperature in a heterogeneous catalytic system.

Biomimetic catalyst, which simulates the basic functions of the enzyme group of oxidoreductase - catalase and monooxygenase, was used as the catalyst here. Characterised by its highly active and selective action these biomimetic catalysts are synthesized based on iron-porphyrin complexes simulating the active component of cytochrome P-450.

Based on this experimental researches, the complex reaction, consisting of parallel-sequential oxidation and dehydrogenation reactions, which are coherently synchronized, proceeds during the process of cyclohexane oxidation with biomimetic catalyst. Depending on the reaction parameters it is possible to deliberately adjust the direction of oxidation reaction and reaction rate.

I. INTRODUCTION

Inducing effect of hydrogen peroxide on synchronous oxidation reaction is accompanied by the occurrence of two interconnected and interacting reactions [1, 2]. The reaction of H_2O_2 decomposition (primary) generates the leading active $^{\bullet}OH$ and $HO_2^{\bullet}$ free radicals in a system. During the interaction of active and free radicals with the substrate, the conversion of the substrate occurs in the secondary reaction, coherently-synchronized with the primary one [3].

The mechanism of such coherently synchronized reactions is being examined in the process of cyclohexane oxidation with hydrogen peroxide in homogeneous and heterogeneous systems. The cyclohexane oxidation is the most commonly studied process, where the valuable for organic synthesis compounds are achieved during oxidative dehydrogenation or during oxidation [4-7]. The implementation of thermodynamically hindered reactions is of great interest for petrochemical and organic synthesis. Among them the reactions of partial dehydrogenation of cyclohexane to cyclohexene and cyclohexadiene should be mentioned.

ΔG, kJ/mol

$$C_6H_{12} \rightarrow C_6H_{10} + H_2 \qquad 39.88$$

$$C_6H_{10} \rightarrow C_6H_8 + H_2 \qquad 115.37$$

It is of course more beneficial in terms of energy to carry out such reactions in conjunction with other reactions, in this case, with the reaction of hydrogen peroxide decomposition.

II. RESULTS AND DISCUSSION

The process of coupling dehydrogenation of cyclohexane to cyclohexene and cyclohexadiene with hydrogen peroxide was carried out without catalyst [8].

The reaction was examined at a temperature range of 450-650 ºC at various flow rates and ratios of starting reactants. The process was of sequential and autocatalytic nature with the period of self-acceleration (kinetic curves for cyclohexadiene and benzene), as shown in Figure 1. Under optimum conditions, the yield of cyclohexene was up to

19.4%, of cyclohexadiene was 3.4% and benzene 2.4%.

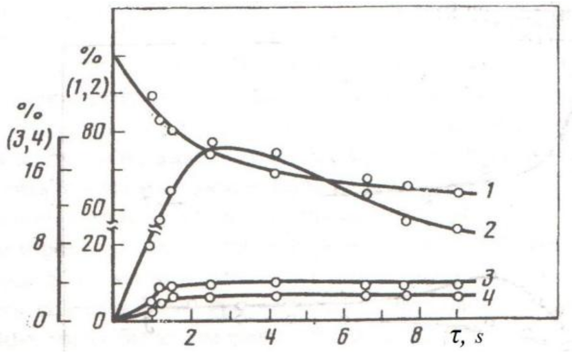


Figure 1. Kinetic curves for coupling dehydrogenation of cyclohexane:

1-cyclohexane; 2-cyclohexene; 3-benzene; 4-cyclohexadiene

Kinetic curves show that the accumulation of cyclohexene as an intermediate product at the initial stage of the process increases up until the rate of its consumption and the rate of accumulation at the conventional contact time equal to τ = 4.2c, becomes equal, and cyclohexene concentration reaches a maximum value. Cyclohexene yield decreases with the further increase in contact time. The rate of formation of cyclohexene and cyclohexadiene initially increases, and reaches its maximum at the inflection point, which is typical for sequential reactions.

At a temperature range of 450-500 ºC the cyclohexene is formed, with the increase in temperature range between 560 ºC and 650 ºC dehydrogenation products contain cyclohexadiene and benzene along with cyclohexene. These data also suggest that with further increase in temperature the ring-opening decomposition reaction of the cyclohexane occurs along with the process of the dehydrogenation. The consequence is the formation of gaseous products such as H_2, CO_2, CH_4, C_2H_4...

These experimental data aggregate show that in the studied range of variations by reaction parameters under the best conditions reaction proceeds in the direction of the oxidative dehydrogenation of cyclohexane achieving the yield of desired products C_6H_{10}, C_6H_8 и C_6H_6 – 19,4%; 3.4% and 2.4% respectively.

It is necessary to identify the nature of the interaction of H_2O_2 with the hydrocarbon, resulting with the formation of unsaturated compound under high-temperature oxidation conditions in order to identify the mechanism of dehydrogenation of cyclohexane.

A prerequisite for the coherently synchronized reactions to proceed in the reaction system is its quantitative characteristic defined by the determinant equation [1]:

$$D = \nu (r_1 / r_{ac} + r_2 / r_{ac})^{-1}$$

where r_1 and r_2 – consumption rate of an actor (H_2O_2) in the primary and secondary reactions respectively, r_{ac} - consumption rate of an acceptor (C_6H_{12}), ν - stoichiometric factor (in our case ν = 1). The value of the determinants calculated by using experimental data D≈0.1 indicates the induced nature of dehydrogenation of cyclohexane.

Under the conditions of the high-temperature cyclohexane gas-phase oxidation with hydrogen peroxide, the reaction proceeds by a free radical mechanism, where active $^{\bullet}OH$ and $HO_2^{\bullet}$ radicals are formed in the primary reaction - in the reaction of H_2O_2 decomposition, and they are consumed in the secondary one - in the dehydrogenation of cyclohexane. Considering that at a high temperature the concentration of $HO_2^{\bullet}$ radicals in the reaction system is much higher than the concentration of $^{\bullet}OH$ radicals [9], the $HO_2^{\bullet}$ radicals play a key role in the mechanism of the dehydrogenation:

chain initiation

$$H_2O_2 \rightarrow 2\,^{\bullet}OH \quad - 217,9 \text{ kJ/mol}$$

chain propagation

$$\begin{cases} H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O + 107,7 \text{ kJ/mol} \\ C_6H_{12} + HO_2^{\bullet} \rightarrow C_6H_{10} + H_2O + {}^{\bullet}OH + 40,17 \text{ kJ/mol} \\ C_6H_{10} + HO_2^{\bullet} \rightarrow C_6H_8 + H_2O + {}^{\bullet}OH + 104,6 \text{ kJ/mol} \\ C_6H_8 + HO_2^{\bullet} \rightarrow C_6H_6 + H_2O + {}^{\bullet}OH + 66,9 \text{ kJ/mol} \end{cases}$$

chain termination

$$\begin{cases} {}^{\bullet}OH + wall \rightarrow {}^{\bullet}OH\ (ads) \\ HO_2^{\bullet} + wall \rightarrow HO_2^{\bullet}(ads) \end{cases}$$

Each successive reaction of oxidative dehydrogenation of cyclohexane is a combination of chain initiation, propagation and termination stages. The system of kinetic equations, adequately describing the experimental data, is as follows [10]:

$$-d[C_6H_{12}]/d\tau = k_{eff\,1}[C_6H_{12}][H_2O_2]$$

$$-d[C_6H_{10}]/d\tau = k_{eff\,1}[C_6H_{12}][H_2O_2] - k_{eff\,2}[C_6H_{10}][H_2O_2]$$

$$-d[C_6H_8]/d\tau = k_{eff\,2}[C_6H_{10}][H_2O_2] - k_{eff\,3}[C_6H_8][H_2O_2]$$

where

$$k_{eff\,1} = 10^{24,9} \exp(-264000\ RT)\, sm^3 / mol \cdot s$$

$$k_{eff\ 2} = 10^{23,9} \exp(-222000 \quad RT) sm^3 / mol \cdot s$$

$$k_{eff\ 3} = 10^{22,8} \exp(-205000 \quad RT) sm^3 / mol \cdot s$$

Examination of the process of coherently synchronized cyclohexane oxidation with hydrogen peroxide was carried out also at a fairly low temperature in a heterogeneous catalytic system. Biomimetic catalyst [11], which simulates the basic functions of the enzyme group of oxidoreductase - catalase and monooxygenase, was used as the catalyst here. Characterised by its highly active and selective action these biomimetic catalysts are synthesized based on iron-porphyrin complexes simulating the active component of cytochrome P-450 [12].

The process of cyclohexane gas phase oxidation was carried out with heterogeneous biomimetic catalysts per-FTPhPFe(III)/Al_2O_3 and PPFe(III)/Al_2O_3 at a temperature of 130 – 250 ºC and a molar ratio C_6H_{12}: H_2O_2 = 1:1.7 with 25% aqueous H_2O_2 solution. The results of these studies are shown in Figure 2.

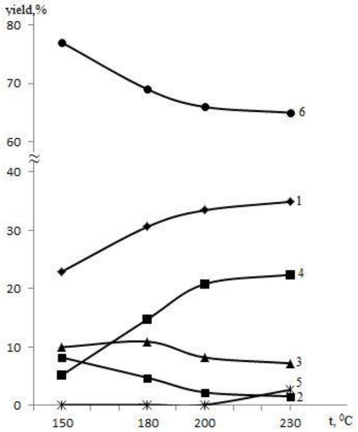


Figure 2. The dependence of the reaction yield of cyclohexane coherently synchronized oxidation with bio simulator per-

Table 1. The dependence of the reaction yield of cyclohexanol coherently synchronized oxidation with bio simulator per-FTPhPFe(III)/Al_2O_3 on the temperature: [H_2O_2]=20%, $v_{H_2O_2}$ =1,41 mL/h, $v_{C_6H_{12}}$ =0,9 mL/h, $C_6H_{11}OH$:H_2O_2=1:1

	Composition of feedstock, %				Composition of obtained reaction yield, %						
t, ^{0}C	$C_6H_{11}OH$	2-methyl cyclohexanol	Hexanoic acid	Hexanoic acid cyclohexyl ester	$C_6H_{11}OH$	C_6H_{10}	1,2 cyclo hexane diol	1,3 cyclohexadiene	2-methyl cyclohexanol	other oxygenates	Conversion
150	97,524	0,481	0,712	0,845	83,921	2,321	2,248	0,105	0,093	9,405	14,079
180	97,524	0,481	0,712	0,845	78,186	7,841	2,875	0,145	0,583	10,753	19,814
200	97,524	0,481	0,712	0,845	67,494	16,688	2,887	0,279	0,295	10,652	30,506
230	97,524	0,481	0,712	0,845	55,255	30,374	2,0	0,1	0,641	10,271	42,745

As shown in Figure 2 at the temperature up to150-160 ºC the reaction that mainly proceeds is cyclohexane oxidation reaction, forming cyclohexanol and cyclohexanone. At the temperature above 180°C the reaction of oxidative dehydrogenation of cyclohexane to cyclohexene (curve 4, Figure 2) begins to accelerate, respectively, the yield of cyclohexanol and cyclohexanone decreases. The sharp increase in the yield of cyclohexene along with the decrease in the yield of formed cyclohexanol indicates that at the temperature of 230 ºC or higher cyclohexanol can also be converted into cyclohexene at lower concentrations of H_2O_2 in the reaction system. This conclusion is confirmed by the results of experimental studies of the process of cyclohexanol oxidation with hydrogen peroxide at a lower concentration (20%) with the biomimetic catalyst, where at elevated temperature (200-230 ºC) the cyclohexene yield is high (16-30%).

The experiments on the effect of the H_2O_2 concentration at a constant temperature (200 ºC) and contact time were conducted. As shown in Figure 3, increased H_2O_2 concentration in the reaction zone contributes to the increase of oxidation reaction rate, which results with the increase of cyclohexanone yield and decrease of cyclohexene yield.

Such results are obtained in a pilot study of cyclohexane oxidation over biomimetic depending on the C_6H_{12} : H_2O_2 ratio at different temperatures.

The results of the effect of the C_6H_{12} : H_2O_2 ratio on the cyclohexane oxidation reaction at a moderate temperature (t = 150 °C), where cyclohexanol and cyclohexanone are the main reaction products are shown in Figure 3.

As it can be seen from the Figure 4 the reaction rate of oxidative dehydrogenation is higher than oxidation reaction rate and the yield of cyclohexane increases at the highest temperature (t = 230 °C).

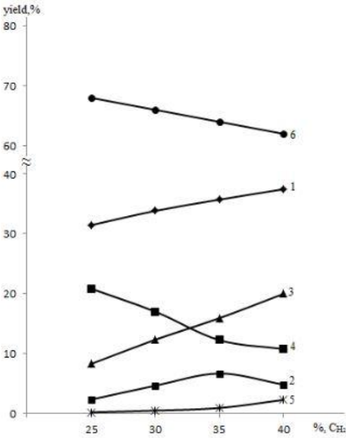


Figure 3. The dependence of the reaction yield of cyclohexane coherently synchronized oxidation with bio simulator per-FTPhPFe(III)/Al_2O_3 on concentration H_2O_2: t=200^0C, $V_{H_2O_2}$ =1,41 mL/h,, $V_{C_6H_{12}}$ =0,9 mL/h,,

1- conversion; 2- cyclohexanol; 3- cyclohexanone; 4- cyclohexene; 5- cyclohexadiene; 6- O_2 yield

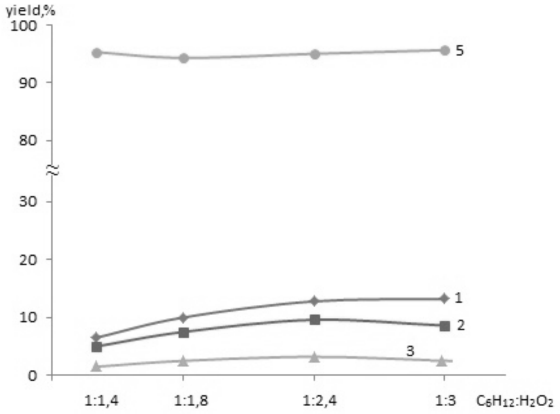


Figure 4. The dependence of the reaction yield of cyclohexane coherently synchronized oxidation over per-FTPhPFe(III)/Al_2O_3catalyst on C_6H_{12} : H_2O_2ratio at the temperature t=150^0C,

$V_{H_2O_2}$ =1,41mL/h,, $V_{C_6H_{12}}$ =0,9mL/h,,

1- conversion; 2- cyclohexanol;
3- cyclohexanone; 4- O2yield

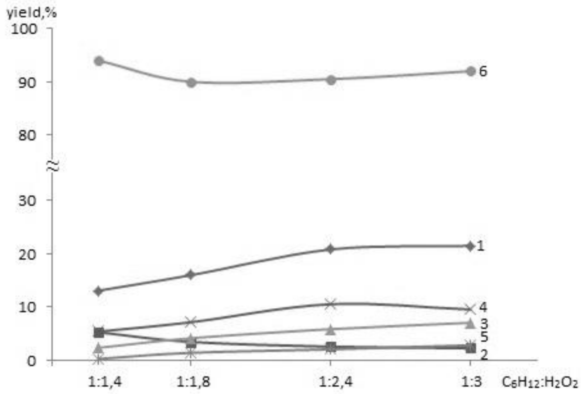


Figure 5. The dependence of the reaction yield of cyclohexane coherently synchronized oxidation over per-FTPhPFe(III)/Al_2O_3catalyst on C_6H_{12} : H_2O_2ratio at the temperature t=230^0C,

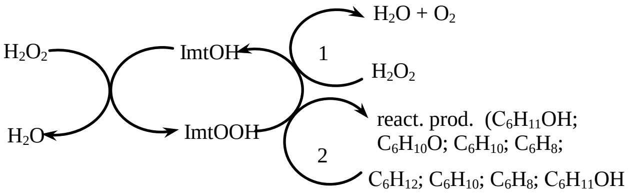
$V_{H_2O_2}$ =1,41mL/h,, $V_{C_6H_{12}}$ =0,9mL/h,,

1- conversion; 2- cyclohexanol; 3- cyclohexanone; 4- cyclohexene; 5- cyclohexadiene; 6- O_2 yield

Thus, the complex reaction, consisting of parallel-sequential oxidation and dehydrogenation reactions, which are coherently synchronized, proceeds during the process of cyclohexane oxidation with biomimetic catalyst. Depending on the reaction parameters it is possible to deliberately adjust the direction of oxidation reaction and reaction rate.

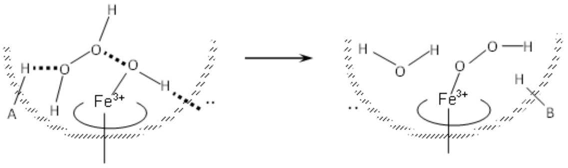
It should be noted that in terms of the mechanism of each stage of this complex reaction of cyclohexane parallel-sequential oxidation with hydrogen peroxide with biomimetics, each oxidation reaction is carried out under inducing effect of hydrogen peroxide intermediates and consists of two coherently synchronized reactions - 1) catalase (H_2O_2 decomposition reaction) and 2) monooxygenase (cyclohexane oxidation reaction) with biomimetic catalyst.

The probable mechanism of cyclohexane coherently synchronized oxidation, considering the parallel-sequential nature of oxidation and dehydrogenation, can be expressed by the general scheme [3]:

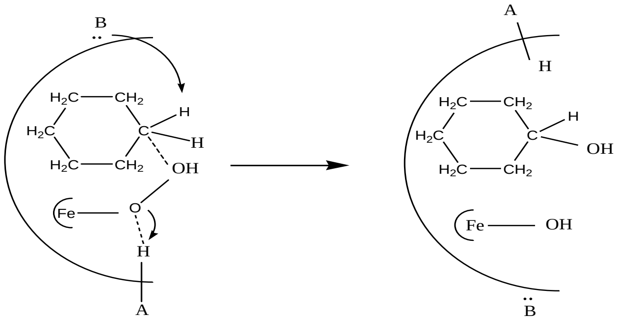


The mechanism of primary and secondary reactions proceeding over biomimetic catalyst is given:

1) Mechanism of catalase reaction



2) The mechanism of reaction of cyclohexane oxidation to cyclohexanol



III. CONCLUSION

The scheme shows that formed active intermediate complex of hydroperoxide (ImtOOH), as in the case of free radical $HO_2^{\bullet}$, is the key active centre for coherent synchronization of catalase (primary) and monooxygenase (secondary) reactions. Coherently synchronized nature of the cyclohexane oxidation reaction follows from the experimental data (Figure 2 and 3). The changes in the catalase reaction rate (curve 6) and the rate of cyclohexane oxidation consumption (curve 1) are shown by the kinetic curves of Figures 2 and 3.

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