REPUBLIC OF AZERBAIJAN

On the rights of the manuscript

ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

COHERENT-SYNCHRONOUS OXIDATION OF CYCLOHEXANE WITH HYDROGEN PEROXIDE

Speciality:	2316.01 – Chemical kinetics and catalysis
Field of science:	Chemistry

Applicant: **Sariyya Alakbar Aghamammadova**

Baku – 2024

The dissertation work was performed in the "Modeling of monooxygenase reactions" laboratory of the "Coherent-synchronized oxidation reactions" department of the Institute of Catalysis and Inorganic Chemistry named after academician M.Nagiyev of Ministry of Science and Education Republic of Azerbaijan

Scientific supervisor:
Doctor of Chemical Sciences,
Academician
Tofik Murtuza Nagiev

Official opponents:
Doctor of Chemical Sciences, Professor
Eldar Isa Akhmedov

Doctor of Chemical Sciences, Professor
Safa Islam Abasov

Ph.D.in Chemistry, Associate Professor
Elvira Anverovna Guseinova

Dissertation council ED 1.15 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at Institute of Catalysis and Inorganic Chemistry named after academician M.Nagiyev of Ministry of Science and Education Republic of Azerbaijan

Chairman of the Dissertation council:
Doctor of Chemical Sciences,
Academician
Dilgam Babir Tagiyev

Scientific secretary of the Dissertation council:
Ph.D.in Chemistry, Associate Professor
Ulviyya Akhmed Mammadova

Chairman of the scientific seminar:
Doctor of Chemical Sciences, Professor
Arif Javanshir Afandi

GENERAL CHARACTERISTICS OF THE WORK

Relevance of the topic and degree of elaboration. Cyclohexanol and cyclohexanone obtained as a result of the oxidation of cyclohexane are valuable chemical products that are widely used in many areas of the chemical industry. Both products are key industrial raw materials in the production of caprolactam and adipic acid, as well as nylon-6 and nylon-6,6 polymers[1]. The demand for increasing their production is constantly increasing. Increasing the production of these compounds can be done both by improving existing production processes and developing new methods.

Cyclohexanol is used in the chemical industry in the production of adipic acid[2] and cyclohexanone, as well as in a number of areas of the national economy: as a solvent for oils, polymers, paints; as a stabilizer for emulsions, lubricants, creams; as an antifoaming and homogenizing agent for disinfectant preparations; as an intermediate for the production of pharmaceutical preparations, plasticizers, cyclohexylamines, pesticides; as a primary product for the production of caprolactam, from which polyamide fiber is made; widely used for the production of cyclohexyl nitrate, which enhances the ignition of diesel fuels.

Cyclohexanone is mainly used as a primary raw material in the production of caprolactam, cyclohexanone oxime and adipic acid, as a solvent for paints, polyvinyl chloride, natural resins, oils, cellulose acetate and nitrocellulose[3].

---

[1] Alnefaie, R.S. Efficient Oxidation of Cyclohexane over Bulk Nickel Oxide under Mild Conditions / R.S. Alnefaie, M. Abboud, A. Alhanash [et al.] // Molecules, – 2022. Vol. 27, Issue 10, – p. 3145-3159.

[2] Lisicki, D. Oxidation of Cyclohexane / Cyclohexanone Mixture with Oxygen as Alternative Method of Adipic Acid Synthesis / D. Lisicki, B. Orlinska, A.A. Marek [et al.] // Materials, – 2023. Vol. 16, Issue 1, – p. 298-307.

[3] Conceicao, N.R. Catalytic cyclohexane oxidation to KA oil using novel hydrosoluble copper (I) complexes bearing aminophosphine ligands: Water as a selectivity promoter / N.R. Conceicao, A.G. Mahmoud, M.F.C. Guedes da Silva [et al.] // Molecular Catalysis, – 2023. Vol. 549, – p. 113512-113523.

The demand for the development of more convenient and efficient methods of obtaining cyclohexanol and cyclohexanone is constantly increasing. Despite the extensive study of the oxidation process of cyclohexane, conducting this process in a new direction with the presence of a biomimetic catalyst with hydrogen peroxide has aroused great interest[4].

Synthesis of cyclohexanol in industry is carried out by hydrogenation of phenol under pressure in the vapor phase with the presence of Pd/Al_2O_3, $Ni/Cr/Al_2O_3$ catalysts; cyclohexanone is obtained from the co-catalytic hydrogenation of cyclohexanol and phenol in the gas phase under pressure.

Conducting the process under pressure with the presence of phenol and hydrogen creates technological difficulties.

Extensive studies have also been conducted on the process of obtaining cyclohexanol and cyclohexanone by oxidation of cyclohexane. As it is known in the work done in this direction, the target products are obtained with low selectivity and very little conversion of cyclohexane.

For this reason, it is an urgent issue to develop new effective catalysts in order to increase its conversion during the oxidation of cyclohexane and increase the selectivity of the process in the direction of cyclohexanone and cyclohexanol.

Recently, in order to carry out chemical processes under milder conditions and with high selectivity, there has been an increase in experimental works in the direction of applying catalysts that reflect the specific functions of enzymes to the processes[5].

---

[4] Pokutsa, A. Sustainable Oxidation of Cyclohexane and Toluene in the Presence of Affordable Catalysts: Impact of the Tandem of Promoter / Oxidant on Process Efficiency / A. Pokutsa, S. Tkach, A. Zaborovsky [et al.] // American Chemical Society, Omega, – 2020. Vol. 5, Issue 13, – p. 7613-7626.

[5] Brehm, J. Enhancing the Chemo-Enzymatic One-Pot Oxidation of Cyclohexane via In Situ H_2O_2 Production over Supported Pd-Based Catalysts / J. Brehm, R.J. Lewis, T. Richards [et al.] // American Chemical Society, Catalysis, – 2022. Vol. 12, Issue 9, – p. 11776-11789.

In this regard, based on the modeling of biochemical processes, the direction of catalysis, which occupies an intermediate position between enzymatic catalysis and chemical catalysis, and is called imitation catalysis, has been developed. In recent years, many works dedicated to modeling and research of active parts of catalase, peroxidase and cytochrome P-450 enzymes have been done in this field.

Research goals and objectives. The aim and task of the dissertation is to study the oxidation reaction of cyclohexane with hydrogen peroxide to cyclohexanol and cyclohexanone on a synthesized new type of biomimetic catalyst: to determine the catalase and monooxygenase activity of the biomimetic catalyst, the kinetic regularities of the biomimetic oxidation reaction of cyclohexane, the study of the mechanism of action of the catalyst, the determination of the coherent-synchronized nature of the reaction and the kinetics consists of research.

Research methods. The following physico-chemical research methods were applied in the implementation of the dissertation: Resonance-Raman spectroscopy, gas chromatography with flame ionization detector (GC-FID), gas chromatography with mass spectrometry detector (GC-MS), methods of determining catalase and monooxygenase activities of the synthesized catalysts.

The main provisions defended are listed below:

- Investigation of catalase activity and antioxidant resistance of heterogeneous biomimetic catalyst perfluorinated iron (III) tetraphenylporphyrin/Al_2O_3 in the reaction of decomposition of H_2O_2 in static system in liquid phase;
- Study of monooxygenase activity and kinetic regularities of the biomimetic catalyst in the cyclohexane oxidation reaction; determination of the coherent-synchronized nature of the reaction based on experimental studies;
- Research in the direction of determining the selectivity and high selectivity towards one of the components of the bioimitator in the reaction of biomimetic monooxidation of cyclohexane to cyclohexanone and cyclohexanol;

- Experimental determination of the routes of conversion of cyclohexane into reaction products, based on the results of experiments, description of the mechanism of electron conversion of these products on the surface of a biomimetic catalyst based on the principle of chain distribution of bonds;
- Kinetic analysis of the coherent-synchronous monooxidation reaction of cyclohexane with H_2O_2 in the presence of a biomimetic catalyst using the determinant equation under chemical interference conditions.

Scientific novelty of the research. For the first time, a heterogeneous-catalytic coherent-synchronized monooxidation reaction of cyclohexane to cyclohexanone and cyclohexanol in a model system consisting of a biomimetic catalyst consisting of a perfluorinated iron (III) tetraphenylporphyrin complex (per-FTPhPFe^{3+}OH/Al_2O_3) immobilized on a solid support (Al_2O_3) and an oxidant (H_2O_2) has been studied. The green oxidant – H_2O_2 and temperature resistant bioimitator per-FTPhPFe^{3+}OH/Al_2O_3 ensured that the reaction proceeded with high conversion and selectivity.

Oxidation-reduction mechanism with the participation of the acid-base centers of the carrier and the functional group of the ligand based on the principle of chain distribution of bonds characteristic of the mechanism of enzymatic catalysis of the oxidation reaction of cyclohexane on the catalyst surface is given.

As a result of the study of the process of oxidation of the mixture of cyclohexane + methylcyclohexane in the presence of a biomimetic catalyst containing iron porphyrin, the high selectivity of the catalyst was determined: only one of the components in the mixture underwent catalytic conversion.

Theoretical and practical significance of research. A new highly efficient method for the oxidation of cyclohexane with hydrogen peroxide in the gas phase to cyclohexanone and cyclohexanol has been developed on the per-FTPhPFe^{3+}OH/Al_2O_3 heterogeneous biomimetic catalyst, which is resistant to the effect of oxidant and high temperature, and has long-term workability. The yields of cyclohexanone and cyclohexanol obtained with high selectivity by this method are 15% and 14%, respectively.

Approval and application. The main results of the dissertation were reported and discussed at the following national and international conferences:

1. 10th Congress on Catalysis Applied to Fine Chemicals (Turku, Finland, 16-19 June 2013)
2. XI European Congress on Catalysis (Lyon, France, 1-6 September 2013)
3. Akademik M.F. Nağıyevin 105 illiyinə həsr olunmuş Respublika Elmi Konfransı (Bakı, 2013)
4. 34th International Conference on Solution Chemistry (Prague, Czech Republic, 30th August – 3rd September 2015)
5. Academic Science Week – 2015 International Multidisciplinary Forum (Baku, Azerbaijan, 2-4 November 2015)
6. APCBEES Rome Conference Abstract (Rome, Italy, 1-3 February 2016)
7. MATEC Web of Conferences, 6th International Conference on Chemistry and Chemical Process (ICCCP 2016) (Rome, Italy, 1-3 February 2016)
8. 22nd International Congress of Chemical and Process Engineering CHISA (Prague, Czech Republic, 27-31 August 2016)
9. 6th EuCheMS Chemistry Congress (Seville, Spain, 11-15 September 2016)
10. Akademik M.Nağıyev adına Kataliz və Qeyri-üzvi Kimya İnstitutunun 80 illik yubileyinə həsr olunmuş Respublika Elmi Konfransı (Bakı, Azərbaycan, 15-16 noyabr 2016)
11. EUROPACAT 2017. 13th European Congress on Catalysis – A bridge to the future (Florence, Italy, 27-31 August 2017)
12. 1st International Conference on Reaction Kinetics, Mechanisms and Catalysis (Budapest, Hungary, 6-9 June 2018)
13. 9th World Congress on Green Chemistry and Technology (Amsterdam, Netherlands, 17-19 September 2018)

14. Akademik M.Nağıyevin 110 illiyinə həsr olunmuş “Nağıyev qiraətləri” elmi konfransı (Bakı, Azərbaycan, 2018)
15. 50th General Assembly & 47th IUPAC World Chemistry Congress (Paris, France, 5-12 July 2019)
16. 5th International Conference on Bioinspired and Biobased Chemistry and Materials (Nice, France, 12-14 October 2020)
17. РОСКАТАЛИЗ IV Российский Конгресс по Катализу (Казань, Россия, 20-25 сентября 2021)

The name of the organization where the dissertation work was performed. The dissertation work was carried out in the "Monooxygenase reaction modeling" laboratory of the "Coherent-synchronized oxidation reactions" department of the Institute of Catalysis and Inorganic Chemistry named after academician Murtuza Nagiyev of the Ministry of Science and Education Republic of Azerbaijan

The structure and scope of the dissertation work. Dissertation work is organized from introduction, four chapters and conclusions. The total volume of the dissertation work, including 44 figures, 4 tables and 255 citied references consists of 150 computer printed sheets and 162960 symbols.

Publication rate of research work. 24 scientific works were published on the subject of the dissertation work. 7 of them are articles, 17 conference materials and thesis. 2 of the articles were published by a single author, and 4 were published in periodical scientific publications included in international summarizing and indexing systems. 13 of thesis have been published in the materials of international and 4 national scientific conferences.

The author’s personal contribution is reflected in the formulation of the purpose of the dissertation, the determination of the methodological approach for its solution, the implementation of experimental studies, the analysis of reaction products in gas-liquid and mass chromatographs, the analysis of the obtained results, the calculation and generalization, as well as the writing of scientific works and the dissertation.

MAIN CONTENTS OF THE WORK

In the introduction, the relevance of the subject of the dissertation is justified, the purpose of the work is mentioned, the scientific innovation of the conducted research, and the theoretical and practical significance of the obtained results are noted.

In the first chapter, the current state of research in the field of cyclohexane oxidation was reviewed, known methods of obtaining cyclohexanone and cyclohexanol were discussed and a comparative analysis was carried out. This chapter includes a literature review about metalporphyrin containing catalytic systems, and based on the results of the literature review, the direction of scientific research is justified.

In the second chapter, the description of the experimental facility where the research was carried out, the methods of preparing biomimetic catalysts, the characteristics of the used reagent (starting substance) and the reaction products, and the methods of analysis were presented. The rules for conducting experiments are reflected in this chapter.

In the third chapter, the results of the experimental study of monooxidation of cyclohexane on the per-FTPhPFe^{3+}OH/Al$_2$O$_3$ biomimetic catalyst were discussed, and **in the fourth chapter,** the mechanism of action of the biomimetic catalyst and the kinetic analysis of the reaction were discussed.

A brief overview of the discussion in chapter three

Experimental study of the kinetic regularities of the gas-phase monooxidation reaction of cyclohexane by H$_2$O$_2$ over a biomimetic catalyst

The heterogeneous catalytic biomimetic monooxidation reaction of cyclohexane by hydrogen peroxide in the gas phase was carried out at atmospheric pressure and in a flowing quartz reactor with a reaction zone of 3 cm^3 (d=1.8 cm) (Figure 1). The structure of the reactor ensures that H$_2$O$_2$ enters the reaction zone without decomposition [13, 14]. Also, the study of the kinetic regularities of the process in a wide range of process parameters: in the temperature range of 130-230°C, in the volume rates of cyclohexane and hydrogen peroxide of 0.3-1.5ml/h and in concentrations of 20-40% of the aqueous solution of H_2O_2, C_6H_{12}:H_2O_2=1:1÷1:3 mol ratio was carried out. 2 types of mixtures of cyclohexane and its derivatives were used as raw materials: 1) 88.85% C_6H_{12}, 6.25% $C_6H_{11}OH$ and 2.53% $C_6H_{11}CH_3$ and 2) 45,4% C_6H_{12}, 1,91% $C_6H_{11}OH$ and 38.64% $C_6H_{11}CH_3$ [5, 11].

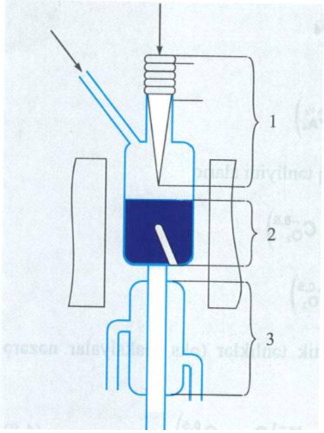


Figure 1. Schematic of a quartz reactor. 1 – heating zone, 2 – reaction zone, 3 – cooling zone[6]

Quantitative and qualitative analysis of the reaction products was performed on Agilent Technology 5975 MSD + 7820 GC mass chromatograph and 7820A gas-liquid chromatograph.

The experimental data obtained as a result of the gas phase monooxidation reaction of cyclohexane by hydrogen peroxide on per-FTPhPFe^{3+}OH/Al_2O_3 biomimetic catalyst are shown in the following pictures.

Figure 2 shows the temperature dependence of the yield of products of the reaction of biomimetic monooxidation of cyclohexane by hydrogen peroxide in the gas phase.

---

[6] Nagiev, T.M. Coherent Synchronized Oxidation Reactions by Hydrogen Peroxide / Tofik M. Nagiev. – Amsterdam: Elsevier, – 2007. – 325 p.

As can be seen from the picture, the oxidation of cyclohexane to cyclohexanol and cyclohexanone occurs at a relatively high rate at a temperature of 130-180°C. As can be seen from Figure 2, the increase in the yield of cyclohexene at a temperature of 200-230°C occurs with a decrease in the yield of cyclohexanol (curves 2 and 4), which gives rise to the possibility that cyclohexene is obtained as a result of the dehydration of cyclohexanol [17, 19].

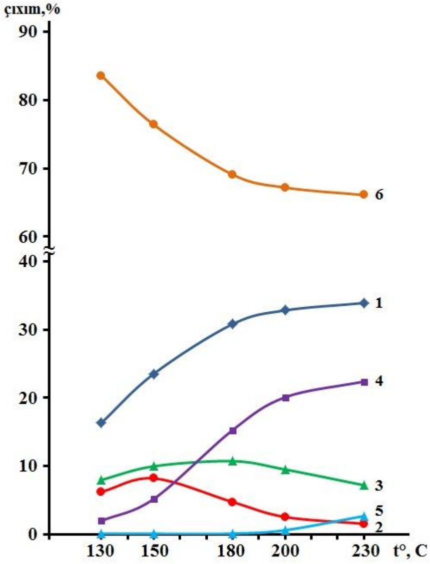


Figure 2. Temperature dependence of the yield of cyclohexane oxidation reaction products by hydrogen peroxide on per-FTPhPFe^{3+}OH/Al_2O_3 biomimetic in a mixture consisting of 88.85% C_6H_{12}, 6.25% $C_6H_{11}OH$ and 2.53% $CH_3C_6H_{11}$: $c_{H_2O_2} = 25\%$, $V_{H_2O_2} = 1.41$ ml/h, $V_{C_6H_{12}} = 0.9$ ml/h, C_6H_{12}:H_2O_2=1:1.5 [17, 19].
1 - conversion C_6H_{12}; 2 - cyclohexanol; 3 - cyclohexanone; 4 - cyclohexene;
5 - 1,3- cyclohexadiene; 6 - consumption of H_2O_2 in the catalase reaction

At this time, the highest yield of cyclohexanone was 10.74% at a temperature of 180°C. A high yield of cyclohexanol was observed at 150°C, 8.23%. The yield of cyclohexene increased from 5.2% to 22.4% with increasing temperature.

Also, from the characteristics of the kinetic curves of 2 and 3, it can be concluded that the formation of cyclohexanone probably does not proceed with the acquisition of cyclohexanol as an intermediate product [21].

In Figure 2, the kinetic curves showing the consumption of H_2O_2 in the catalase reaction (curve 6) and the conversion of the substrate – cyclohexane (curve 1) are synchronous. Thus, interaction and coherence are also observed between these synchronous reactions. For example, the maximum rate of catalase reaction corresponds to the minimum rate of cyclohexane conversion (monoxidation reaction) (130°C), the minimum rate of catalase reaction corresponds to the maximum rate of cyclohexane conversion (230°C). This shows the coherent-synchronized nature of the reaction of biomimetic monooxidation of cyclohexane by H_2O_2 [12].

In this context, the kinetic data obtained in figure 2 are theoretically and experimentally shown in [17, 19]. At the same time, it was noted that such a reaction system is effective in coherent-synchronized conditions.

Since the dominant (target) product in our research is cyclohexanone (Figure 2) and its relatively high yield (10.74%) was observed at 180°C, studies were conducted to study the effect of contact time on the oxidation process of cyclohexane at this temperature.

From the kinetic curves reflecting the results of this study (Figure 3), it can be seen that when the contact time (τ) in the monooxidation reaction of cyclohexane increases to 10 seconds, the yield of cyclohexanone first increases (up to 15.2%), and then remains stable and almost does not change. The conversion of cyclohexane increases linearly with increasing contact time, while the recovery of cyclohexene also increases as a function of contact time. The kinetic patterns shown in Figure 3 lead us to conclude that cyclohexanone is probably not derived from cyclohexanol. It should be noted that in the absence of cyclohexane, H_2O_2 completely decomposes during this contact period [17, 19].

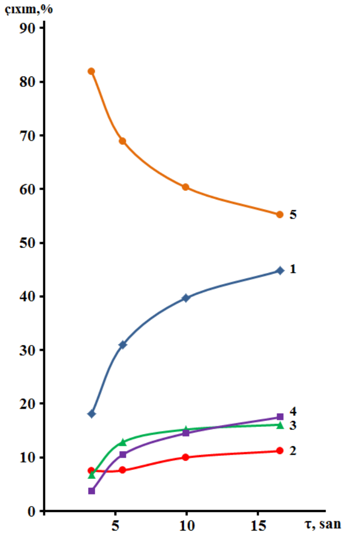


Figure 3. Dependence of the contact time (τ) of the yield of the reaction products of cyclohexane oxidation on per-FTPhPFe^{3+}OH/Al_2O_3 biomimetic in a mixture consisting of 88.85% C_6H_{12}, 6.25% $C_6H_{11}OH$ and 2.53% $CH_3C_6H_{11}$: t=180°C, $c_{H_2O_2} = 25\%$, C_6H_{12}:H_2O_2=1:1 [17, 19].

1 - conversion C_6H_{12};
2 - cyclohexanol;
3 - cyclohexanone;
4 - cyclohexene;
5 - consumption of H_2O_2 in the catalase reaction

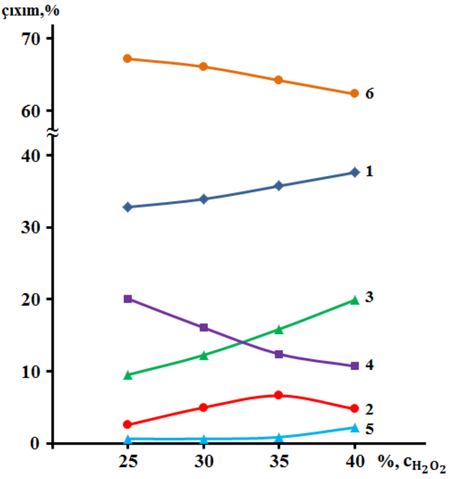


Figure 4. Dependence of the yield of cyclohexane oxidation reaction products on per-FTPhPFe^{3+}OH/Al_2O_3 biomimetic in a mixture consisting of 88.85% C_6H_{12}, 6.25% $C_6H_{11}OH$ and 2.53% $CH_3C_6H_{11}$ on the concentration of H_2O_2 in aqueous solution: t=200°C, $V_{H_2O_2} = 1.41$ ml/h, $V_{C_6H_{12}} = 0.9$ ml/h [17, 19].

1 - conversion C_6H_{12};
2 - cyclohexanol; 3 - cyclohexanone;
4 - cyclohexene; 5 - 1,3- cyclohexadiene;
6 - consumption of H_2O_2 in the catalase reaction

The effect of the concentration of hydrogen peroxide in water solution on the monooxidation process of cyclohexane is illustrated in figure 4. A very interesting fact can be observed here: the increase of concentration of H_2O_2 has little effect on the conversion of cyclohexane, and the consumption of H_2O_2 in the catalase reaction does not change much in the interval of concentration of H_2O_2, despite its high character. Nevertheless, changing the concentration of H_2O_2 leads to a significant increase in the yield of cyclohexanone. From the kinetic curves of formation of monooxidation products - cyclohexanone and cyclohexanol, it can be seen that the yield of cyclohexanone increases from 10% to 19%, and the yield of cyclohexanol increases to 7% ($c_{H_2O_2} = 35\%$), then decreases. Increasing the concentration of H_2O_2 has a negative effect on the yield of cyclohexene, causing its yield to decrease from 20% to 10% [17, 19, 23].

Study of the process of oxidation of cyclohexanol by hydrogen peroxide

In order to specify the mechanism of biomimetic conversion of cyclohexane to cyclohexanone, the oxidation process of cyclohexanol obtained as an intermediate product on the same bioimitator under the same conditions was studied [21].

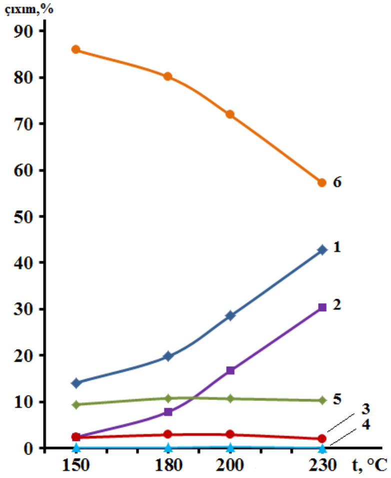


Figure 5. Temperature dependence of the yield of cyclohexanol oxidation reaction by hydrogen peroxide on per-FTPhPFe^{3+}OH/Al_2O_3 biomimetic catalyst: $c_{H_2O_2} = 20\%$, $V_{H_2O_2} = 1.41$ ml/h, $V_{C_6H_{11}OH} = 0.9$ ml/h [21]
1 - conversion $C_6H_{11}OH$; 2 - cyclohexene; 3 - 1,2- cyclohexanediol; 4 - 1,3-cyclohexadiene; 5 - other oxygen compounds; 6 - consumption of H_2O_2 in the catalase reaction

From the kinetic curves depicted in Figure 5, it can be seen that the formation of cyclohexanone, that is, the peroxidase reaction of cyclohexanol, is not observed, the main reaction product is cyclohexene.

It should be noted that the increase in the conversion of cyclohexanol with the increase in temperature from 150°C to 230°C sharply increases the rate of formation of cyclohexene. At the same time, a decrease in the speed of the catalase reaction is observed from the kinetic curves, synchronously with the consumption rate of cyclohexanol. This indicates the presence of interaction and connection between the reactions [17, 19].

Thus, the kinetic data in Figures 2 and 5 reveal the mechanism of formation of cyclohexanol and cyclohexene. Indeed, from the kinetic data of Figure 2, it can be seen that up to a temperature of 130-180°C, the process of monooxidation of cyclohexane mainly takes place, and at a temperature above 180°C, the dehydration of cyclohexanol to cyclohexene accelerates (Figure 2 curve 4), accordingly, the yield of cyclohexanol decreases. A sharp increase in the yield of cyclohexene, parallel to a decrease in the yield of the formed cyclohexanol, shows that at a temperature of 230°C (figure 2) and at lower concentrations of H_2O_2 (figure 4), the conversion of cyclohexanol into cyclohexene occurs. This result is unequivocally confirmed by the experimental data of the oxidation of $C_6H_{11}OH$ at a temperature of 200-230°C on a biomimetic catalyst: cyclohexanol is completely dehydrated with the formation of cyclohexene (16-30%) with a high yield (Figure 5) [17, 19].

The composition mentioned above was also confirmed during coherent-synchronous oxidation of pure raw material (fixanal) consisting of 96% cyclohexane by hydrogen peroxide over per-FTPhPFe^{3+}OH/Al_2O_3 catalyst. For comparison, we have presented the results of our experiments with a small amount of pure raw materials in figure 6.

As can be seen from the picture (picture 6), the formation of cyclohexanol and cyclohexanone proceeds according to parallel reactions (150-200°C). At a higher temperature, the yield of cyclohexene increases. At this time, as we mentioned in the pictures above, the output of cyclohexanol decreases sharply and the curves take an S-shaped shape (picture 6, curves 2 and 4). This again indicates that cyclohexene is formed by dehydration of cyclohexanol at high temperature.

Also, the results of our experiments with pure fixanal almost repeat the results of our experiments with a mixture consisting of 88.85% C_6H_{12}, 6.25% $C_6H_{11}OH$ and 2.53% $C_6H_{11}CH_3$.

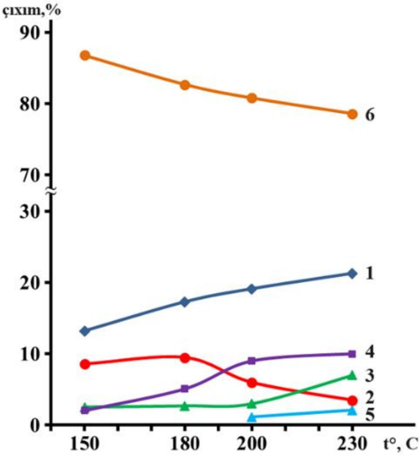
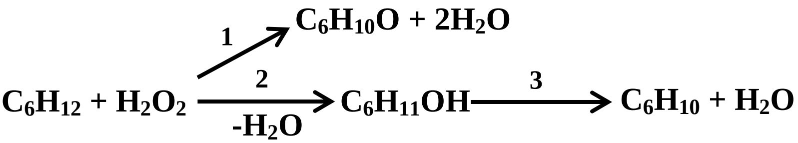


Figure 6. Temperature dependence of the yield of the products of the coherent-synchronous oxidation reaction of the pure raw material containing 96% C_6H_{12} with H_2O_2 over the per-FTPhPFe^{3+}OH/Al_2O_3 catalyst: : $c_{H_2O_2} = 25\%$, $V_{H_2O_2} = 1.41$ ml/h, $V_{C_6H_{12}} = 0.41$ ml/h, $C_6H_{12}:H_2O_2=1:3$
1 - conversion C_6H_{12}; 2 - cyclohexanol; 3 - cyclohexanone; 4 - cyclohexene;
5 - 1,3- cyclohexadiene; 6 - consumption of H_2O_2 in the catalase reaction

Thus, based on the experimental data in pictures 2, 3, 4, 5, and 6, we can note that the conversion of cyclohexane into cyclohexanol, cyclohexanone, and cyclohexene proceeds by a series-parallel mechanism, and we can present this mechanism with the scheme in picture 7:



$$\begin{tikzcd} & C_6H_{10}O + 2H_2O & \\ C_6H_{12} + H_2O_2 \arrow[ur, "1"] \arrow[r, "2", "-H_2O"'] & C_6H_{11}OH \arrow[r, "3"] & C_6H_{10} + H_2O \end{tikzcd}$$

Figure 7. Scheme of conversion of cyclohexane to cyclohexanol, cyclohexanone and cyclohexene [23]

Parallel formation of cyclohexanone and cyclohexanol according to reaction 1 and 2 occurs synchronously with the sequential formation reaction of cyclohexene (Figure 7).

Comparing the kinetic curves of cyclohexene production in Figures 2, 3, 4, 5 and 6, it can be concluded that at temperatures higher than 180°C and relatively small concentrations of H_2O_2, cyclohexene is formed by sequential reactions 2 and 3 (Figure 7).

Study of the selectivity of the biomimetic catalysts containing iron porphyrin in the oxidation reaction of cyclohexane and mixtures of cyclohexane with its derivatives

The next stage of the research was the study of the selective effect of the biomimetic catalytic system against mixtures of cyclohexane with its derivatives [11].

The results of studies using raw materials containing 88.85% C_6H_{12}, 6.25% $C_6H_{11}OH$ and 2.53% $C_6H_{11}CH_3$ show that mainly cyclohexane undergoes conversion during the oxidation process, while the amount of methylcyclohexane in the raw materials practically does not change [11].

In order to specify the selective effect of biomimetic catalysts containing iron porphyrin in the process of oxidation of complex mixtures against only one component, an artificial mixture containing 45.4% C_6H_{12}, 38.64% $C_6H_{11}CH_3$, 1.91% $C_6H_{11}OH$ was taken. The results of the oxidation process of this mixture with 20% hydrogen peroxide at different temperatures and hydrogen peroxide delivery rates on $PPFe^{3+}OH/Al_2O_3$ biomimetic are given in the following tables. According to the data in Tables 1 and 2, a clear conclusion is drawn about the selective effect of the biomimetic catalyst against the oxidation of cyclohexane even in the mixture with a sufficiently high amount of methylcyclohexane (38.64%).

Thus, the studied biomimetic catalyst has not only high selectivity, but also selectivity towards the oxidizing substrate, which, as a rule, is characteristic only of monooxygenase enzymes.

The high selectivity and catalytic activity of the biomimetic catalyst can be explained by the fact that the cyclohexane-biomimetic complex formed during the reaction (unlike methyl cyclohexane) can imitate the monooxygenase cyclohexane-enzyme complex.

Table 1.

The results of the process of cyclohexane oxidation in the mixture by hydrogen peroxide on the PPFe^{3+}OH/Al$_2$O$_3$ biomimetic:
$c_{H_2O_2} = 20\%$, $V_{H_2O_2} = 1.41$ ml/h, $V_{C_6H_{12}} = 0.9$ ml/h [11]

t, °C	Composition of raw material, %				Composition of the obtained reaction product, %						Conv., %	Cons. of H_2O_2 in catalase reac. %
	C_6H_{12}	$C_6H_{11}CH_3$	$C_6H_{11}OH$	$C_6H_{10}(CH_3)_2$	C_6H_{12}	$C_6H_{11}CH_3$	$C_6H_{11}OH$	$C_6H_{11}O$	C_6H_{10}	$C_6H_{10}(CH_3)_2$		
150	45.44	**38.64**	1.91	5.48	35.09	**38.93**	0.64	3.45	6.26	6.77	10.35	89
180	45.44	**38.64**	1.91	5.48	31.28	**39.31**	1.85	4.24	8.07	7.08	14.16	86
200	45.44	**38.64**	1.91	5.48	27.44	**38.58**	2.79	5.72	9.50	7.17	18.0	82
220	45.44	**38.64**	1.91	5.48	22.94	**38.63**	2.50	7.50	12.5	6.70	22.5	77

Table 2.

The results of the process of cyclohexane oxidation in the mixture by hydrogen peroxide on the PPFe^{3+}OH/Al$_2$O$_3$ biomimetic:
$c_{H_2O_2} = 20\%$, $V_{C_6H_{12}} = 0.9$ ml/h, t=150°C

$V_{H_2O_2}$	Composition of raw material, %				Composition of the obtained reaction product, %						Conv., %	Cons. of H_2O_2 in catalase reac. %
	C_6H_{12}	$C_6H_{11}CH_3$	$C_6H_{11}OH$	$C_6H_{10}(CH_3)_2$	C_6H_{12}	$C_6H_{11}CH_3$	$C_6H_{11}OH$	$C_6H_{11}O$	C_6H_{10}	$C_6H_{10}(CH_3)_2$		
0.9	45.44	**38.64**	1.91	5.48	38.11	**38.36**	0.65	2.27	4.41	8.04	7.32	92
1.41	45.44	**38.64**	1.91	5.48	35.09	**38.93**	0.64	3.45	6.26	6.77	10.34	89
1.8	45.44	**38.64**	1.91	5.48	24.33	**38.44**	2.37	11.11	7.63	8.64	21.1	79
2.05	45.44	**38.64**	1.91	5.48	14.44	**38.53**	9.50	14.0	7.5	6.8	31	69
2.25	45.44	**38.64**	1.91	5.48	16.44	**37.90**	6.00	15.5	7.5	7.0	29	71

A brief overview of the discussion in chapter four

In this chapter, the most likely mechanism of the coherent-synchronized monooxidation of cyclohexane with hydrogen peroxide in the gas phase over the per-FTPhPFe^{3+}OH/Al$_2$O$_3$ heterogeneous biomimetic catalyst was considered, and the unity of oxidation-reduction and acid-base mechanisms was determined in this mechanism.

Based on the mechanisms, a kinetic analysis of the monooxygenase reaction of the oxidation of cyclohexane with hydrogen peroxide on the per-FTPhPFe^{3+}OH/Al$_2$O$_3$ biomimetic was carried out based on the experimentally observed kinetic regularities.

The kinetic analysis of the process of biomimetic oxidation of cyclohexane with hydrogen peroxide was carried out using the determinant equation.

Mechanism of coherent-synchronized oxidation reaction of cyclohexane by H_2O_2

The process of biomimetic oxidation of cyclohexane by hydrogen peroxide is carried out in the BioImtOH – H_2O_2 – C_6H_{12} system in the bifurcation mode, where catalase (decomposition of hydrogen peroxide) and monooxygenase (monooxidation of cyclohexane) reactions simultaneously take place. A graphic representation of this process is clearly depicted in the infographic in figure 8, which provides complete and clear information about the entire process [21].

As can be seen from the infographic (figure 8) [21], three interrelated reactions take place in the presented system, and these reactions interact with each other on the surface of the biomimetic catalyst and interact with each other. Coherence (interaction) between the synchronous reactions in the system occurs due to the active intermediate BioImtOOH formed as a result of the interaction of hydrogen peroxide with the biomimetic catalyst in the primary reaction - catalase reaction. The processed intermediate is consumed in the coherent-synchronized catalase and monooxygenase reactions with the formation of the end products of the respective reactions and the complete recovery of the biomimetic catalyst at the end of the catalytic cycle. The final products of the catalase reaction are molecular oxygen and water, and the final products of the parallel monooxygenase reactions are cyclohexanone and cyclohexanol. Other reaction products cyclohexene, cyclohexadiene are formed as a result of sequential conversion of the products obtained in parallel reactions[7,8].

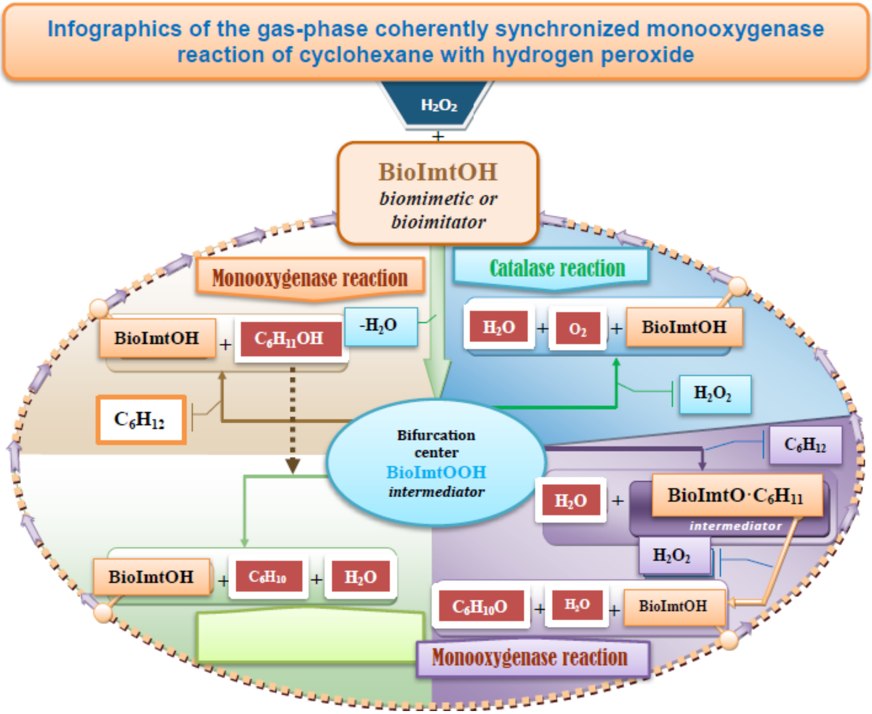


Figure 8. Infographic of the coherent-synchronized monooxygenase reaction of cyclohexane by hydrogen peroxide in the gas phase [21][7,8]

---

[7] Нагиев, Т.М. Сопряженные реакции в контексте современных идей / Тофик М. Нагиев. – Баку: Şərq-Qərb, – 2020. – 208 с.

[8] Nağıyev, T.M. Sinxron reaksiyalara koherent baxış / Tofiq M. Nağıyev. – Bakı: Şərq-Qərb, – 2018. – 216 s.

The generalized scheme of the coherent-synchronized monooxidation reaction of cyclohexane by hydrogen peroxide is described as follows [19]:

Figure 9. Generalized scheme of the coherent-synchronized monooxidation reaction of cyclohexane with hydrogen peroxide [19]

It can be seen from Figure 9 that in this type of catalytic systems, the bioimimator has a catalytic effect on two coherent synchronous reactions. Both synchronized reactions occur in the presence of the common intermediate ImtOOH. The interaction of H_2O_2 with the biomimetic in the initial reaction forms a highly active hydroperoxide active center (Figure 10), and the interaction of this center with both H_2O_2 and cyclohexane leads to the formation of the main products by a mechanism based on the principle of chain distribution of bonds: I – O_2 and H_2O in the 2nd stage of the catalase reaction (Figure 11) and cyclohexanol and cyclohexanone in the II reaction (Figures 12 and 13) [8, 9].

Both reactions depicted in Figure 9 occur through the common intermediate per-FTPhPFe^{3+}OOH/Al_2O_3, which transfers the inductive effect of the first reaction to the second reaction, that is, the process proceeds in the bifurcation mode.

The mechanism of action of the two complex reactions is based on the idea that the reaction of decomposition of hydrogen peroxide (primary reaction) accelerates the reaction of monoxidation of cyclohexane, which is the second reaction, and vice versa, the second reaction slows down the formation of the products of the first reaction.

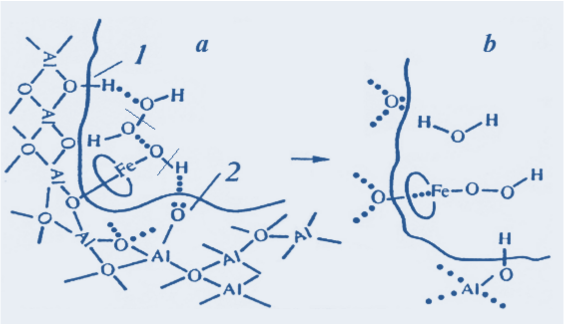


Figure 10. The formation mechanism of the mimic-substrate complex[6,9]
a - interaction of the active ligand with H_2O_2 in the presence of Al_2O_3 acid and base centers on ImtOH;
b - active intermediate – mimic-substrate complex (ImtOOH/Al_2O_3).
1 - acid center;
2 - base center;
┼ **and ··· accordingly, the breakdown and establishment of communication**

Figure 10 shows the formation mechanism of the ImtOOH complex as a result of the interaction of H_2O_2 with per-FTPhPFe^{3+}OH/Al_2O_3 biomimetic, similar to the formation of the Chance complex (PPFe^{3+}OOH) under the influence of catalase enzyme[6,9]. In this case, Al_2O_3, which is used as an acid-base matrix, performs the function of protein.

It can be seen from the scheme of the presented mechanism of the catalase reaction that under the influence of the axial group of the Fe^{3+}OH ligand, as well as with the help of the acid and base centers of the carrier, the separation of two protons from the acid center and the hydroxyl group of the ligand, as a result of one-way transfer of protons and the movement of electrons in the opposite direction, the breaking of bonds and new H_2O_2 is transformed into an active intermediate (ImtOOH) within the framework of the principle of chain distribution of bonds with the formation of bonds[6].

---

[9] Нагиев, Т.М. Химическое сопряжение / Т.М. Нагиев. – Москва: Наука, – 1989. – 216 с.

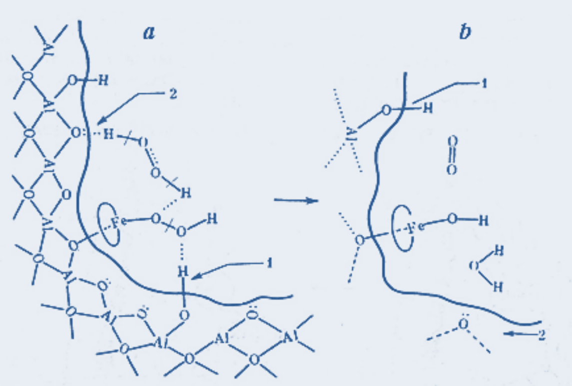


Figure 11. Mechanism of formation of catalase reaction products[6,9]
a - interaction of the mimic-substrate complex with the second H_2O_2 molecule;
b - formation of H_2O and O_2, recovery of the catalyst;
1 - acid center;
2 – base center.
┼ and ··· accordingly, the breakdown and establishment of communication

According to these ideas, H_2O_2 forms the per-FTPhPFe^{3+}OOH/Al_2O_3 active complex as a result of heterolytic action, and this complex can be used in two directions: by interacting with the second hydrogen peroxide molecule, forming the end products of the catalase reaction (Figure 11) or monooxidizing cyclohexane . Stable products of the catalytic cycle are formed by the "assistance" of acid and base groups and the functional group of the ligand on the Al_2O_3 carrier, and then these products are separated from the catalyst.

According to the elementary first stage (Fig. 11), by attracting the proton of the hydroxyl group of the Fe(III)OOH ligand of hematin, transferring the electron to the oxygen atom, the O–H bond is broken and a water molecule is formed. At this time, as a result of the effect of the electrons gathered around Fe–O: on the proton of the H–O–O–H molecule and the combined effect of the base center of the carrier, the O–H bonds in the H_2O_2 molecule are broken with the formation of O=O, a free oxygen molecule is released. Thus, the interaction of the intermediate with the second molecule of H_2O_2 leads to the formation of the end products of the catalase reaction, as is known[6].

The probable mechanism of the monooxidation reaction of cyclohexane to cyclohexanol on a biomimetic catalyst can be described as follows [21]:

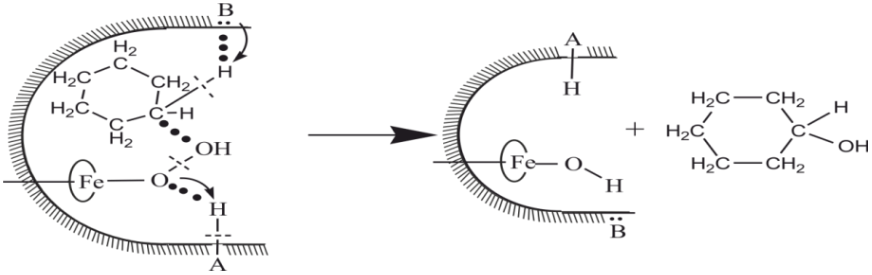


Figure 12. Mechanism of monooxidation of cyclohexane to cyclohexanol [21]. A - acid center; B - base center.

As can be seen from the mechanism, the proton of the Brensted acid center of the carrier moves to the oxygen of the O-OH ligand, and this event is accompanied by the breaking of the O-OH bond and the combination of the OH residue with the carbon atom, which, in turn, is accompanied by the detachment of the proton with the participation of the Lewis base centers of the carrier (Figure 12). The entire sequence of electron and proton transitions takes place in the communication distribution system practically as the same time and with little energy consumption.

As can be seen from the experimental data, the peroxidase reaction does not occur, in which case we can describe the probable mechanism of the formation of cyclohexanone from cyclohexane as follows [23]:

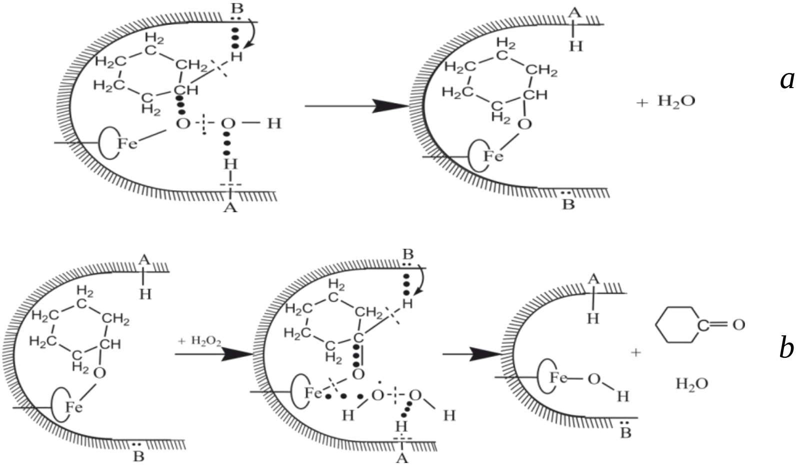


Figure 13. Mechanism of monooxidation of cyclohexane to cyclohexanone [23] A - acid center; B - base center.

According to the experimental results and presented schemes (Figure 13, a and b), the direct conversion of cyclohexane into cyclohexanone proceeds with the formation of the intermediate biomimetic-substrate complex Imt-O-C_6H_{11}, which is formed by the interaction of the intermediate (ImtOOH) with cyclohexane (Figure 13, a). The interaction of this complex with another H_2O_2 molecule leads to an oxidative-reductive transformation of the complex, resulting in cyclohexanone, water and the initial biomimic (Figure 13, b). This mechanism is compatible with the formation of cyclohexanone with heavier H_2O_2 (30% and higher) and at lower temperatures (150-180°C).

As can be seen from the mechanisms of biomimetic monooxidation of cyclohexane with hydrogen peroxide (Figures 12, 13), the acid-base centers of the carrier (Al_2O_3) play a key role in the formation of reaction products. Aluminum oxide, which has amphoteric properties, acts as an electron donor and acceptor, thereby helping to break and form bonds [20, 23].

Determining the coherent-synchronous characteristics of the reaction through the determinant equation

The inductive effect of hydrogen peroxide, which is used as an oxidant in the reaction of biomimetic oxidation of cyclohexane, causes chemical interference in the reaction system - a system of connected reactions[7,8].

It is known that the formation of chemical induction in the system of connected reactions takes place with the participation of three leading components: actor (A), inductor (In) and acceptor (Acc). The strengthening of the activity of the reaction between the actor and the acceptor is related to the transformation of the third component (In) into the system into a highly reactive particle that easily reacts with the actor (A) and the acceptor (Acc).

$\mathbf{A + In \rightarrow X \rightarrow SM}$ first reaction

$\mathbf{X + Acc \rightarrow SM}$ second reaction

X - intermediate active particle, SM - final product

The transformation of the actor into an active form and its subsequent transformation into the final product is the first reaction, and the interaction of the active particle into which the actor is transformed with the acceptor is the second reaction.

The inductive effect of H_2O_2 causes H_2O_2 to play the role of both an oxidizing agent and an inductor introducing active particles into the system in connected reactions with its participation. For this reason, oxidation reactions with H_2O_2 create two-component coupled reaction systems[7,8].

$\mathbf{A + A(In) \rightarrow X \rightarrow SM}$ first reaction

$\mathbf{A + Acc \rightarrow SM}$ second reaction

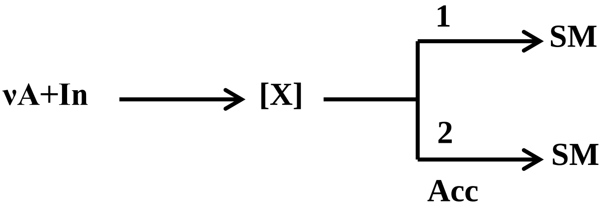
In such variant, both obvious and non-obvious participation of the actor in the second reaction is possible. We can more clearly express the indicated reaction, the transformation of any compound with H_2O_2:

$$\underset{\text{actor}}{\mathbf{H_2O_2}} + \underset{\text{inductor}}{\mathbf{H_2O_2}} \rightarrow \left[\mathbf{\dot{O}H,\ H\dot{O}_2}\right] \rightarrow \mathbf{H_2O + O_2} \qquad \text{I reac.}$$

$$\underset{\text{actor}}{\mathbf{H_2O_2}} + \underset{\text{acceptor}}{\mathbf{RH}} \rightarrow \mathbf{ROH\ \text{və}\ RO\ (reaction\ products)} \qquad \text{II reac.}$$

Apparently, the active radicals introduced by hydrogen peroxide into the reaction system ($\dot{O}H$ and $H\dot{O}_2$) interact with the primary compound and ensure its easy conversion.

The mechanism of chemical bonding can be visualized more clearly in a generalized scheme as follows:



In gas-phase oxidation reactions with H_2O_2 in the presence of a catalyst, chemical induction occurs through the active intermediate complex formed by H_2O_2 with the catalyst. The theory of coupled reactions was once again developed on the basis of the long-term research conducted by Academician T. Nagiev and his colleagues on biomimetic catalytic oxidation processes with H_2O_2. Based on his analysis of the reactions connected with a new approach, T. Nagiev determined that there is not one-sided, but mutual coherence in the reactions connected to biological systems in the imitation catalysis system with H_2O_2.

The above-mentioned monooxygenase reactions are coherently related to the initial reaction of H_2O_2 decomposition, and the coherent-synchronous occurrence of these reactions can be characterized quantitatively and qualitatively by means of the determinant factor (D). The determinant factor is calculated using the following equation:

$$\boldsymbol{D = \nu\left(\frac{f_{A_1}}{f_{Acc}} + \frac{f_{A_2}}{f_{Acc}}\right)^{-1}}$$

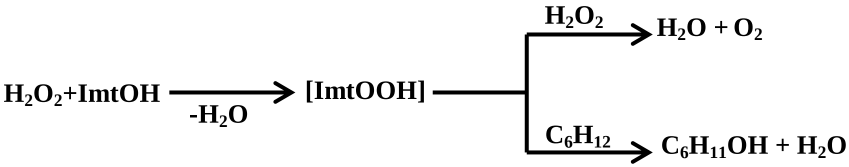
As can be seen from Figure 9, hydrogen peroxide is used as an intermediate in two coherent-synchronous reactions: the first catalase (1) is consumed in the amount of f_{A_1}, and the second monooxygenase (2) is consumed in the amount of f_{A_2}. The consumption of cyclohexane (acceptor) is denoted by f_{Acc}. ν is the stoichiometric coefficient of the actor.

H_2O_2 decomposition and cyclohexane monooxidation coherent-synchronous reactions can be shown from the point of view of connected (coupling) reactions as follows:

$$\underset{\text{actor}}{\mathbf{H_2O_2}} + \underset{\text{inductor}}{\mathbf{H_2O_2}} = \mathbf{2H_2O + O_2} \tag{1}$$

$$\underset{\text{actor}}{\mathbf{H_2O_2}} + \underset{\text{acceptor}}{\mathbf{C_6H_{12}}} = \mathbf{C_6H_{11}OH + H_2O} \tag{2}$$

Here, H_2O_2 is the actor, consumed in both reactions (1) and (2), the second H_2O_2 molecule is the inductor, cyclohexane is the acceptor, and the products of the second reaction (2) are formed from its interaction with hydrogen peroxide. A more visual scheme of these reactions in the presence of a biomimetic catalyst can be described as follows:



The calculated values of the determinant, as well as information about the coherence ratio according to the following equation, are given in table 3:

$$f^0_{H_2O_2} = f^1_{1H_2O_2} + f^1_{2H_2O_2} = f^2_{1H_2O_2} + f^2_{2H_2O_2} = \cdots = const,$$

This indicates that the observed reactions are indeed coherent-synchronized.

$$0.0072 = 0.0054 + 0.0018 = 0.0052 + 0.0020 = \cdots = const$$

Table 3.

Determinant values of cyclohexane monooxidation reaction.
$c_{H_2O_2} = 25\%$, C_6H_{12}:H_2O_2=1:1

t°, C	$V_{C_6H_{12}}$, ml/h	$V_{H_2O_2}$, ml/h	τ, sec	Conv. C_6H_{12}, %	$N^0_{C_6H_{12}}$, mol/h	$N^0_{H_2O_2}$, mol/h	f_{A_1}, mol/h	f_{A_2}, mol/h	f_{Acc}, mol/h	D
150	0.3	0.3	17.75	38.5	0.0028	0.0024	0.0015	0.0009	0.0009	**0.45**
150	0.5	0.5	10.65	36.6	0.0046	0.0040	0.0026	0.0014	0.0014	**0.42**
150	0.9	0.9	5.92	28.16	0.0083	0.0072	0.0054	0.0018	0.0018	**0.33**
150	1.5	1.5	3.55	12.93	0.0139	0.0120	0.0111	0.0009	0.0009	**0.15**
180	0.3	0.3	16.57	44.8	0.0028	0.0024	0.0013	0.0011	0.0011	**0.52**
180	0.5	0.5	9.94	39.7	0.0046	0.0040	0.0025	0.0015	0.0015	**0.46**
180	0.9	0.9	5.52	31.05	0.0083	0.0072	0.0052	0.0020	0.0020	**0.36**
180	1.5	1.5	3.31	18.1	0.0139	0.0120	0.0104	0.0016	0.0016	**0.21**
200	0.3	0.3	15.87	38.4	0.0028	0.0024	0.0015	0.0009	0.0009	**0.45**
200	0.5	0.5	9.52	37.9	0.0046	0.0040	0.0025	0.0015	0.0015	**0.44**
200	0.9	0.9	5.29	32.6	0.0083	0.0072	0.0050	0.0022	0.0022	**0.38**
200	1.5	1.5	3.17	18.1	0.0139	0.0120	0.0104	0.0016	0.0016	**0.21**
230	0.3	0.3	14.92	38.4	0.0028	0.0024	0.0015	0.0009	0.0009	**0.45**
230	0.5	0.5	8.95	37.4	0.0046	0.0040	0.0027	0.0013	0.0013	**0.43**
230	0.9	0.9	4.97	34.5	0.0083	0.0072	0.0050	0.0022	0.0022	**0.40**
230	1.5	1.5	2.98	22.31	0.0139	0.0120	0.0098	0.0022	0.0022	**0.26**

As can be seen from the table, the values obtained for the determinant factor are within the condition of conjucated reactions (0<D<1) on the chemical interference scale (Figure 14)[10].

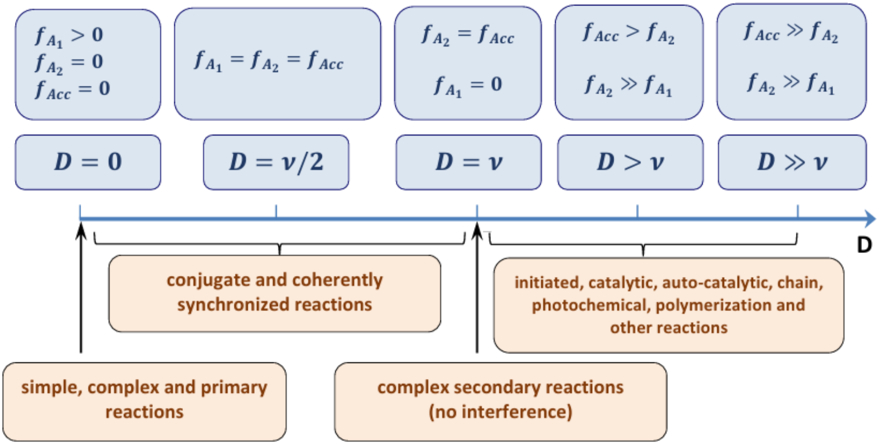


Figure 14. Chemical interference determinant scale[10]

---

[10] Nagiev, T.M. Conjugated Reactions in Chemistry and Biology in the Context of Modern Ideas / Tofik M. Nagiev. – Generis Publishing, – 2021. – 171 p.

Thus, the fact that these reactions are coherent-synchronous (D<1) allows us to control the speed and direction of these complex-targeted reactions, as is known. So, for example, if we mainly need to obtain monooxidation products - cyclohexanol and cyclohexanone, and the values of the corresponding determinant are small, then by manipulating other conditions of the reaction, by maintaining this small value, the process can be effectively directed in the direction of monooxidation. With the help of factor D, favorable conditions for obtaining cyclohexanol and cyclohexanone were determined. In Table 3, these conditions are as follows: when D=0.42: t=150°C, τ=10.65 seconds, C_6H_{12}:H_2O_2=1:1, and the yield of monooxidation reaction products is 27.3% (cyclohexanol - 14.1%, cyclohexanone - 13.2%) contane.

Also, from table 3, the value of the determinant for the conversion of cyclohexane to cyclohexene under the studied conditions is D=0.45, this value corresponds to the conditions where cyclohexene is obtained more efficiently (t=230°C, τ=14.92 sec, C_6H_{12}:H_2O_2=1:1, cyclohexene deduction - 27.2%). By manipulating the value of factor D, the process can be directed towards both monooxidation and cyclohexene production. In addition, the D factor allows to determine the potential possibility of obtaining a certain product (targeted) with a higher yield in the second reaction. For example, if we want to increase the value of D to 0.6 in order to direct the process towards the production of cyclohexene, then by substituting this value in the determinant equation, we can determine the ratio of starting reagents and the consumption of H_2O_2 in the first and second reaction. This will help us determine the conditions for achieving higher yields of the target product, cyclohexene. The solution of the determinant equation with the calculation of the rate constants and activation energy within the framework of the kinetic equations of the rate of two coherent-synchronized reactions will allow creating a kinetic model of the cyclohexane conversion process according to the general scheme in Figure 15 [19].

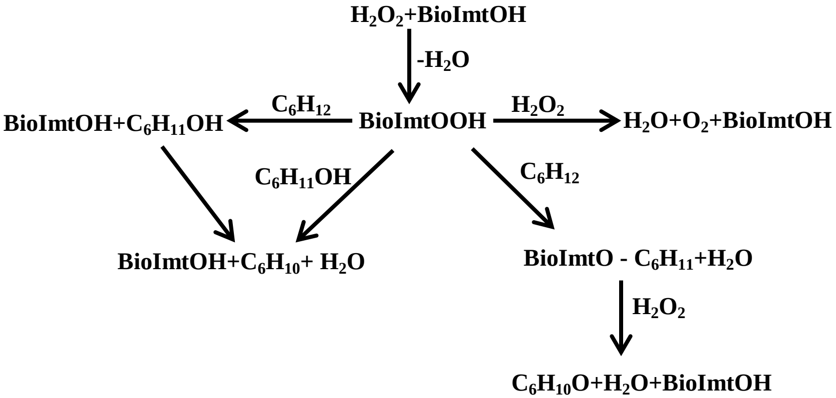


Figure 15. General scheme of the cyclohexane conversion process [19]

Finally, note that the determinant equation for a chemical system consisting of coherent-synchronized (primary and secondary (target)) reactions adequately reflects the experimental results.

RESULTS

1. During the study of the catalase activity of the synthesized heterogeneous biomimetic catalyst containing iron porphyrin per-FTPhPFe^{3+}OH/Al_2O_3, high catalase activity in the decomposition reaction of H_2O_2, high resistance to temperature and oxidant effects of this catalyst were determined [2, 4].
2. Based on the experimental study of the kinetic regularities of the heterogeneous catalytic monooxidation reaction of cyclohexane with hydrogen peroxide over per-FTPhPFe^{3+}OH/Al_2O_3, the coherent-synchronized nature of the two reactions occurring in the system - catalase and monooxygenase reactions was shown [6, 13, 17].
3. The optimal conditions for the maximum yield of the target products were determined: a) during the τ=14.67 seconds contact time, at 130°C temperature, the concentration of the hydrogen peroxide solution in water 25%, in the molar ratio

$C_6H_{12}:H_2O_2=1:1$ the yield of cyclohexanone was 11% (cyclohexanol - was 8.3%). Selectivity for monooxygenase reaction products is 90% (selectivity for cyclohexanone is 51%). b) during the $\tau=6.21$ seconds contact time, at 130°C temperature, the concentration of the hydrogen peroxide solution in water 25%, in the molar ratio $C_6H_{12}:H_2O_2=1:1$ the yield of cyclohexanol was 13% (cyclohexanone - 4.3%). Selectivity for monooxygenase reaction products is 99% (selectivity for cyclohexanol is 75%) [17, 19, 21, 23].

4. Mechanisms of conversion of cyclohexane to cyclohexanol, cyclohexanone and cyclohexene on the surface of biomimetic catalyst based on the principle of chain distribution of bonds were presented, and the unity of oxidizing-reducing and acid-base mechanisms was described in this mechanism [17, 19].
5. In the reaction of oxidation of cyclohexanol by hydrogen peroxide over the per-FTPhPFe^{3+}OH/Al$_2$O$_3$ biomimetic catalyst, cyclohexanone was not obtained. On the contrary, cyclohexene was obtained with a high yield. This indicates that in the monooxidation of cyclohexane, cyclohexanone is not obtained from cyclohexanol, which is an intermediate product, but cyclohexanone and cyclohexanol are obtained from cyclohexane by parallel reactions [21].
6. During the study of the process of biomimetic monooxidation of a mixture of cyclohexane and its derivatives by hydrogen peroxide, the high selectivity of the bioimitator against one component was determined [5, 10, 11, 15].
7. The kinetic analysis of the process of heterogeneous catalytic monooxidation of cyclohexane with hydrogen peroxide on the per-FTPhPFe^{3+}OH/Al$_2$O$_3$ biomimetic catalyst was carried out using the determinant equation, and the coherent-synchronous character of the reaction was once again confirmed [24].

The main results of the dissertation work are published in the following scientific works:

1. Aghamammadova, S., Nagieva, I., Gasanova, L. [et al.]. Oxidation of cyclohexane by hydrogen peroxide on heterogeneous biomimetic catalyst // 10th Congress on Catalysis Applied to Fine Chemicals, – Turku, Finland: – 16-19 June, – 2013, – p. 50.
2. Aghamammadova, S., Nagieva, I., Gasanova, L. [et al.]. Biomimetic catalysts for catalase, peroxidase and monooxigenase reactions // XI European Congress on Catalysis, – Lyon, France: – 1-6 September, – 2013, – poster 2-T6-269.
3. Гасанова, Л.М., Нагиева, И.Т., Агамамедова, С.А. Окисление циклогексана пероксидом водорода на биомиметическом катализаторе // Akademik M.F.Nağıyevin 105 illiyinə həsr olunmuş elmi konfransın materialları, – Bakı: – 2013, I cild, – s. 58-60.
4. Nagiev, T., Gasanova, L., Aghamammadova, S. [et al.]. Heterogenous bioimitators of catalase reaction // 34th International Conference on Solution Chemistry, – Prague, Czech Republic: – 30th August – 3rd September, – 2015, – P42, – p. 34.
5. Ağaməmmədova, S.A. Tsikloheksanın hidrogen peroksidlə oksidləşməsi prosesində biomimetik katalizatorun seçiciliyinin tədqiqi // Academic Science Week – 2015 International Multidisciplinary Forum, – Baku: – 2-4 November, – 2015, – p. 108-110.
6. Aghamammadova, S., Nagieva, I., Gasanova, L. [et al.]. Kinetics and Mechanism of the Reaction of Coherently Synchronized Oxidation and Dehydrogenation of Cyclohexane by Hydrogen Peroxide // 2016 APCBEES Rome Conference Abstract, – Rome, Italy: – 1-3 February, – 2016, – B0017 Presentation 6, – p. 45.
7. Aghamammadova, S., Nagieva, I., Gasanova, L. [et al.]. Kinetics and Mechanism of the Reaction of Coherently Synchronized Oxidation and Dehydrogenation of Cyclohexane by Hydrogen Peroxide // MATEC Web of Conferences, 6th International Conference on Chemistry and Chemical Process (ICCCP 2016), – Rome, Italy: – 1-3 February, – 2016, Vol. 49, 01002, published by

EDP Sciences

8. Aghamammadova, S., Nagieva, I., Gasanova, L. [et al.]. The mechanism of oxidative conversion of cyclohexane on heterogeneous biomimetic catalyst // 22nd International Congress of Chemical and Process Engineering CHISA 2016, – Prague, Czech Republic: – 27-31 August, – 2016, – P3. – p. 38
9. Nagiev, T., Gasanova, L., Aghamammadova, S. [et al.]. Hydrogen peroxide dissociation on sustainable biomimetic catalysts // 6th EuCheMS Chemistry Congress, – Seville, Spain: – 11th-15th September, – 2016, Congress Program, Short Oral, Abstract 723.
10. Агамамедова, С.А., Гасанова, Л.М., Нагиев. Т.М. Избирательное действие биомиметического катализатора в процессе окисления пероксидом водорода // M.Nağıyev adına Kataliz və Qeyri-Üzvi Kimya İnstitutunun 80 illik yubileyinə həsr olunmuş Respublika Elmi Konfransının MATERİALLARI, – Bakı: – 15-16 noyabr, – 2016, – s. 273-274.
11. Агамамедова, С.А. Избирательное действие биомиметического катализатора в процессе окисления пероксидом водорода / С.А.Агамамедова, Л.М.Гасанова, Т.М.Нагиев // Азербайджанский Химический Журнал, – Баку: – 2016. №4, – с. 19-23.
12. Aghamammadova, S.A. Kinetics and Mechanism of the Reaction of Coherently Synchronized Oxidation and Dehydrogenation of Cyclohexane by Hydrogen Peroxide / S.Aghamammadova, I.Nagieva, L.Gasanova [et al.] // International Journal of Engineering Research and Application, – 2017. Vol. 7, №2, – p. 36-40.
13. Aghamammadova, S., Nagieva, I., Gasanova, L. [et al.]. Coherently Synchronized Oxidation of Cyclohexane by Hydrogen Peroxide on Biomimetic Catalyst per-FTPhPFe(III)OH/Al_2O_3 // EUROPACAT 2017. 13th European Congress on Catalysis – A bridge to the future, – Florence, Italy: – 27-31 August, – 2017, Book of Abstracts.
14. Aghamammadova, S.A. Coherently synchronized oxidation and dehydrogenation of cyclohexane by hydrogen peroxide /

S.A.Aghamammadova, I.T.Nagieva, L.M.Gasanova [et al.] // Azerbaijan Chemical Journal, – Baku: – 2017. №3, – s. 6-11.

15. Aghamammadova, S., Nagieva, I., Gasanova, L. [et al.]. Selectivity of a biomimetic catalyst in the process of oxidation of cyclohexane by hydrogen peroxide in the mixture with its derivatives // 1st International Conference on Reaction Kinetics, Mechanisms and Catalysis, – Budapest, Hungary: – 6-9 June, – 2018, p. 55-56.
16. Aghamammadova, S., Nagieva, I., Gasanova, L. [et al.]. Mechanism of biomimetic monooxidation of cyclohexane by hydrogen peroxide // 9th World Congress on Green Chemistry and Technology, – Amsterdam, Netherlands: – 17-19 September, – 2018, – p. 64.
17. Aghamammadova, S.A. Coherent-Synchronized Biomimetic Monooxidation of Cyclohexane by Hydrogen Peroxide / S.A.Aghamammadova, I.T.Nagieva, L.M.Gasanova [et al.] // Journal of Physical Chemistry A, – Moscow: – 2018. Vol. 92, №12, – p. 2455-2463.
18. Агамамедова, С.А., Нагиева, И.Т., Гасанова, Л.М. Механизм реакции когерентно-синхронизированного окисления циклогексана пероксидом водорода на биомиметике per-FTPhPFe(III)OH/Al_2O_3 // Akademik M.Nağıyevin 110 illiyinə həsr olunmuş “Nağıyev qiraətləri” elmi konfransının materialları, – Bakı, – 2018, – s. 154.
19. Aghamammadova, S.A. Catalytic Monooxidation of Cyclohexane by Hydrogen Peroxide in Gas-phase / Sariyya Aghamammadova, Inara Nagieva, Latifa Gasanova [et al.] // The Journal of Reaction Kinetics, Mechanisms and Catalysis, – 2019. Vol. 126, №2, – p. 701-715.
20. Aghamammadova, S., Nagieva, I., Gasanova, L. [et al.]. Selectivity of the Iron (III) Porphyrin Catalyst in the Monooxidation Reaction of Cyclohexane by Hydrogen Peroxide // 50th General Assembly & 47th IUPAC World Chemistry Congress, – Paris, France: – 5-12 July, – 2019, – P.1309.
21. Aghamammadova, S.A. Peculiarities of Cyclohexane Oxidation

Mechanism by Means of “Green Oxidizer” Hydrogen Peroxide on per-FTPhPFe^{3+}OH/Al_2O_3 // – Baku: Chemical Problems, – 2020. Vol. 18, №1, – p. 20-25.

22. Aghamammadova, S., Nagieva, I., Gasanova, L. [et al.]. Heterogeneous biomimetic catalyst for oxidation of cyclohexane // 5th International Conference on Bioinspired and Biobased Chemistry and Materials, – Nice, France: – 12-14 October, – 2020, VIRTUAL
23. Aghamammadova, S.A. Mechanism of biomimetic oxidation of cyclohexane to cyclohexanone by hydrogen peroxide // – Baku: Azerbaijan Chemical Journal, – 2021. №1, – p. 61-66.
24. Агамамедова, С.А., Нагиева, И.Т., Гасанова, Л.М. [и др.]. Биомиметическое монооксидирование циклогексана пероксидом водорода // РОСКАТАЛИЗ IV Российский Конгресс по Катализу, – Казань, Россия: – 20-25 сентября, – 2021, – с. 568-569.

The defense will be held on 13 june 2024 at 10^{00} at the meeting of the Dissertation Council ED 1.15 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at the Institute of Catalysis and Inorganic Chemistry named after academician M.Nagiyev of Ministry of Science and Education Republic of Azerbaijan.

Address: AZ 1143, Baku city, H.Javid Avenue, 113.

Dissertation is accessible at the library of the Institute of Catalysis and Inorganic Chemistry named after academician M.Nagiyev of Ministry of Science and Education Republic of Azerbaijan.

Electronic versions of dissertation and its abstract are available on the official website (www.kqkiamea.az) of the Institute of Catalysis and Inorganic Chemistry named after academician M.Nagiyev of Ministry of Science and Education Republic of Azerbaijan.

Abstract was sent to the required addresses on 13 may 2024.

Signed for print: 07.05.2024

Paper format: $60\times84^{1/16}$

Volume: 38 270 signs

Number of hard copies: 20