UDC 544.4;544.47:544.344

PECULIARITIES OF CYCLOHEXANE OXIDATION MECHANISM BY MEANS OF “GREEN OXIDIZER” HYDROGEN PEROXIDE ON per-FTPhPFe^{3+}OH/Al_2O_3

S.A. Aghamammadova

Acad. M.Nagiyev Institute of Catalysis and Inorganic Chemistry, ANAS
H.Javid Ave.,113, AZ 1134, Baku, Azerbaijan
e-mail: aghamammadova@yahoo.com

Received 20.11.2019

Abstract: *In the process of gas-phase coherently synchronized oxidation of cyclohexane by hydrogen peroxide in the presence of a heterogeneous biomimetic catalyst per-FTPhPFe^{3+}OH/Al_2O_3, the reaction products were cyclohexanol, cyclohexanone and cyclohexene. An experimental study aimed at clarifying the routes of cyclohexane conversion into cyclohexanone and cyclohexene made it possible to determine mechanisms for producing cyclohexanone and cyclohexene. The study went to show that the conversion of cyclohexane into cyclohexanone takes no place through the formation of cyclohexanol, and the formation of cyclohexene occurs by dehydration of cyclohexanol. The mechanism of cyclohexanone formation is manifest through the formation of an intermediate biomimetic - substrate complex Imt-O-C_6H_{11} which is formed as a result of intermediate (ImtOOH) interaction with cyclohexane.*

Keywords: *hydrogen peroxide, cyclohexane, oxidation, biomimetic catalysts, cyclohexanone, cyclohexanol.*

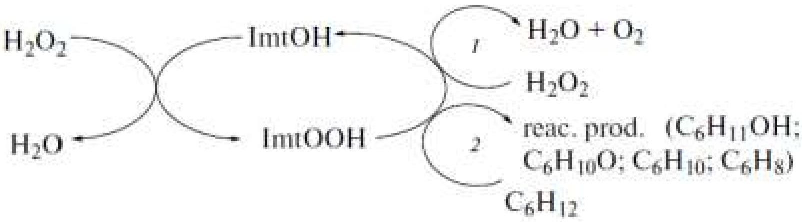
DOI: 10.32737/2221-8688-2020-1-20-25

Introduction

Earlier we explored the gas phase oxidation of cyclohexane by hydrogen peroxide in the presence of a heterogeneous biomimetic catalyst synthesized based on the iron-porphyrin complex, where the reaction products were cyclohexanol, cyclohexanone and cyclohexene [1]. It was established that the biomimetic oxidation of cyclohexane by hydrogen peroxide is a complex and coherently synchronized reaction. Coherently synchronized nature of the process is due to the inducing ability of hydrogen peroxide which contributes to the formation of highly active intermediate complex similar to the enzyme-substrate complex. Hydrogen peroxide is an affordable and cheap “green oxidizer” according to principles of the “Green Chemistry” concept and is increasingly used in hydrocarbon oxidation processes [2, 3].

The generalized scheme of coherently synchronized biomimetic oxidation of cyclohexane by hydrogen peroxide is shown as follows [1, 4-6]:

Scheme I



It follows from the scheme that two interrelated reactions occur in the system of biomimetic oxidation of cyclohexane by hydrogen peroxide: 1) catalase and 2) oxidation of cyclohexane. The relationship between these reactions is formed through the use of highly active complex (ImtOOH) which is formed by interaction of H_2O_2 with bioimitator (ImtOH). The interaction of this active intermediate with the second H_2O_2 molecule in the primary (1) and with cyclohexane in the secondary (2-monooxygenase) reactions leads to the formation of final reaction products.

This study was carried out to determine the routes for the conversion of cyclohexane to reaction products and to examine in detail the mechanisms of formation of the main reaction products, such as cyclohexanol, cyclohexanone and cyclohexene.

Experimental part

Experimental research into the biomimetic oxidation of cyclohexane was carried out in the gas phase in a flowing quartz reactor with reaction zone volume at 3.0 cm^3 at the temperature range of 130-230°C and atmospheric pressure in the presence of biomimetic catalyst with the active part of perfluorinated iron tetraphenylporphyrin backed on a solid Al_2O_3 support. As an oxidizing agent there were used aqueous solutions of hydrogen peroxide of various concentrations (20–40%).

In contrast to the well-known studies on biomimetic oxidation of cyclohexane carried out mainly in the liquid phase, the gas-phase oxidation of cyclohexane on heterogeneous bioimitator, as was shown in [7, 8], has significant advantages: the process is carried out in a flow system with a fixed catalyst layer through more simplified technology where reaction products are not mixed with the catalyst and after the reaction their separation is not required and no additional costs are required.

Analysis of reaction products was carried out on chromium-mass spectrometer 5975 MSD + 7820 GC System and gas-liquid chromatograph 7820A GC System from Agilent Technology and on the chromatograph ЛХМ-80.

Results and discussion

Proceeding from experimental study data, it was found that the conversion of cyclohexane into reaction products (cyclohexanol, cyclohexanone, cyclohexene) occurs in parallel and parallel-sequential reactions. The results of these experiments are presented in Fig. 1 and 2.

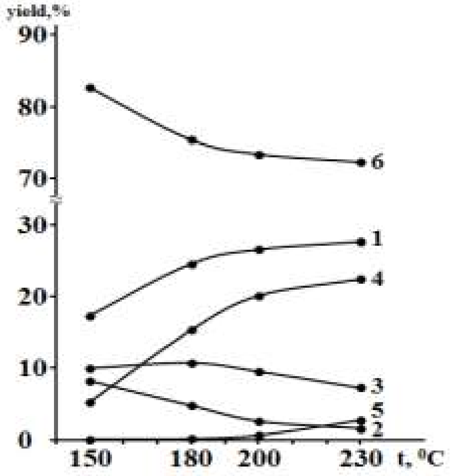


Fig.1. Temperature dependence of the yields of cyclohexane oxidative conversion by hydrogen peroxide in a mixture with 6.25% of $C_6H_{11}OH$ and 2.53% of $CH_3C_6H_{11}$ on per-FTPhPFe(III)/Al_2O_3 biomimetic:

$c_{H_2O_2}$ = 25%, $c_{H_2O_2}$ = 1.41 ml/h,

$V_{C_6H_{12}}$ = 0.9 ml/h, C_6H_{12}: H_2O_2 = 1: 1.5

1 - conversion of C_6H_{12}; 2 - cyclohexanol; 3 - cyclohexanone; 4 - cyclohexene; 5 - cyclohexadiene; 6 - O_2

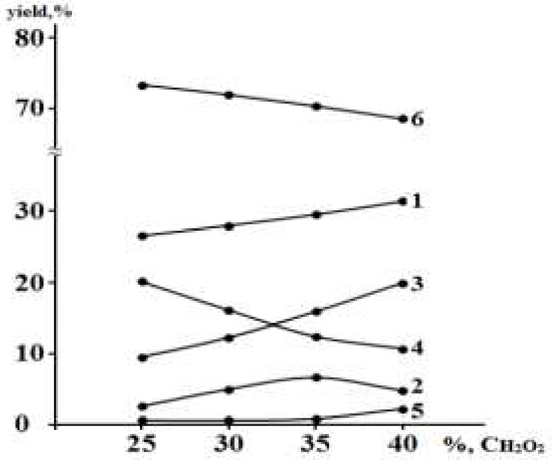


Fig.2. Dependence of the yields of cyclohexane oxidation on per-FTPhPFe(III)/Al_2O_3 bioimitator on the concentration of H_2O_2 in aqueous solution:

t = 200°C, $V_{H_2O_2}$ = 1.41 ml/h,

$V_{C_6H_{12}}$ = 0.9 ml/h

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

As shown in the Fig. 1, oxidation of cyclohexane to cyclohexanol and cyclohexanone proceeds at the highest rate at a temperature range of 150-180°C. As temperature rises, the yield of cyclohexene sharply increases and traces of cyclohexadiene (200-230°C) are detected. At this time the yield of cyclohexanol decreases as temperature rises, and the yield of cyclohexanone at 180° C pass through maximum (10.34% at 180°C). The nature of kinetic curves cannot fully explain mechanisms of reaction products formation. The temperature dependence of the kinetic curves (curves 1 and 6) goes to show that starting from 200°C, the H_2O_2 decomposition into molecular oxygen is stabilized which indicates that hydrogen peroxide in the system is completely consumed for running two interrelated reactions (catalase and monooxygenase). It is shown in [9] that this reaction system is effectively realized in a coherently synchronized regime. The obtained kinetic data (Fig. 1) are in good agreement with the theory and practice of coherently synchronized reactions [5].

The results of the effect of hydrogen peroxide concentration in aqueous solution on monooxidation of cyclohexane show that an increase in the H_2O_2 concentration leads to significant decrease in the yield of cyclohexene and significant increase in the yield of cyclohexanone while the yield of cyclohexanol passes through a maximum (7.6%) (Fig.2).

In order to clarify the routes for the conversion of cyclohexane to reaction products, such as cyclohexanone, cyclohexene and the mechanisms of their formation, was required additional research.

Initial experiments were conducted to explore the conversion of cyclohexanol on biomimetics without the use of H_2O_2. To maintain the same contact time under identical conditions for cyclohexane oxidation reaction by hydrogen peroxide, water was supplied to the system in the amount of an aqueous solution of H_2O_2. At the lowest temperatures (150-180° C), no cyclohexanol conversion was observed, and as temperature rises above 250° C the formation of cyclohexene began.

Thus, experimental studies of cyclohexane oxidation reaction at the highest temperatures with low concentrations of hydrogen peroxide, obtaining of high yields of cyclohexene is explained as being due to the fact that not all active centers (acidic or basic) that exist on the surface of the Al_2O_3 support are coated with the iron-porphyrin complex to play an important role in the dehydration process.

This is also confirmed by the fact that rise in dehydration rate of cyclohexanol with temperatures above 250° C without the use of H_2O_2 corresponds to the known data of the dehydration of cyclohexanol over Al_2O_3 at temperatures of 350-400°C [10].

In order to answer the key question: if cyclohexanone is formed out of cyclohexanol or not, the oxidation reaction of cyclohexanol (97.52% $C_6H_{11}OH$ in the feed) by hydrogen peroxide was studied under identical conditions. Kinetic curves in Fig. 3 show that the peroxidase oxidation reaction of cyclohexanol, that is, the formation of cyclohexanone, is practically not observed. Basically, the dehydration of cyclohexanol into cyclohexene proceeds here.

Experiments with the reaction of biomimetic oxidation of cyclohexane by hydrogen peroxide at high temperatures using H_2O_2 with low concentrations and obtaining of high yields of cyclohexene correspond to the results of dehydration of cyclohexanol without the use of H_2O_2. Therefore, under these conditions, dehydration exceeds the oxidative dehydrogenation reaction.

According to the research results (Fig. 3), we can say that the conversion of cyclohexane into cyclohexanone takes no place through the formation of cyclohexanol. The mechanism of cyclohexanone formation is expressed through the formation of an intermediate biomimetic – substrate complex Imt – O – C_6H_{11} which is formed as a result of intermediate (ImtOOH) interaction with cyclohexane [11]. The interaction of this complex with another H_2O_2 molecule leads to oxidation-reduction transformation of the complex into cyclohexanone, water, and the original biomimic.

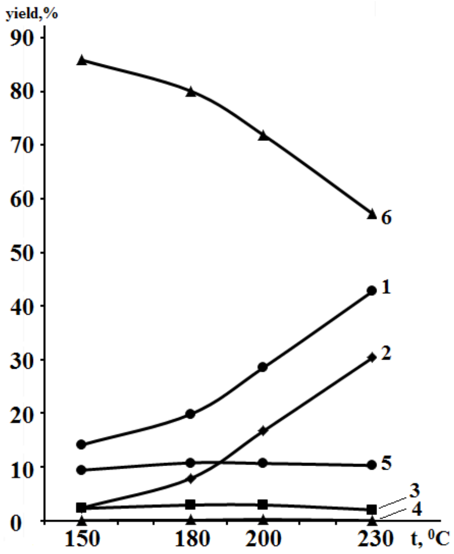
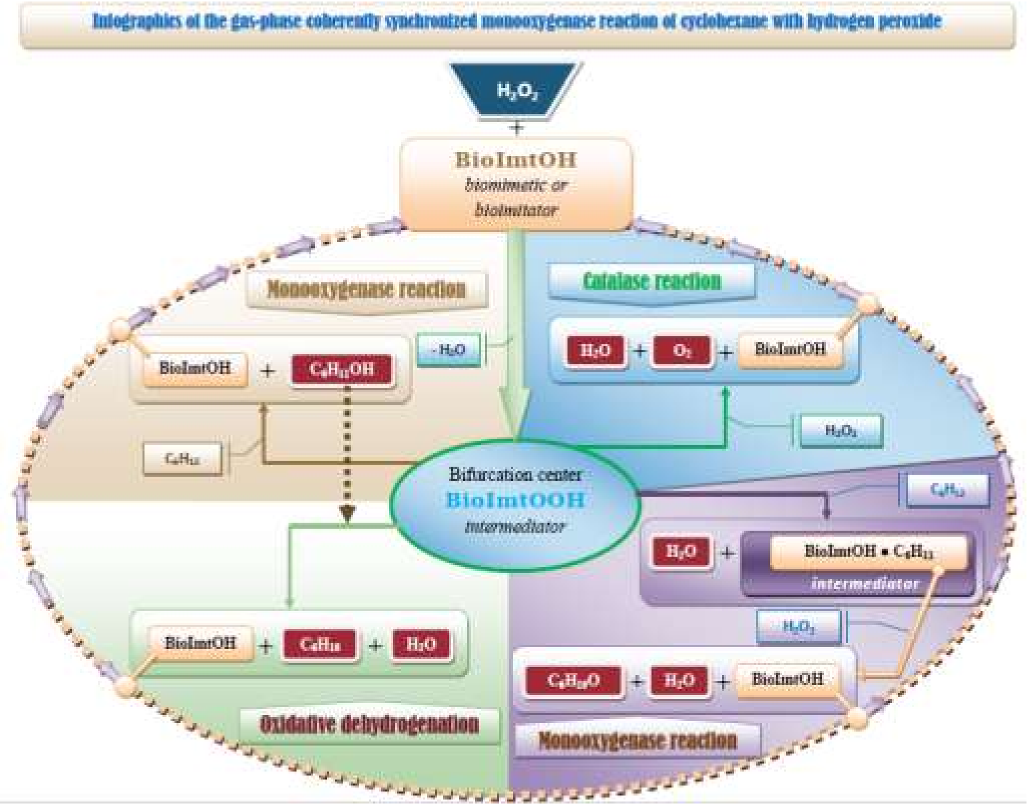


Fig. 3. The yield of cyclohexanol conversion on per-FTPhPFe(III)/Al_2O_3 biomimetic by hydrogen peroxide depending on the temperature:

$c_{H_2O_2}$ = 20%, $V_{H_2O_2}$ = 1.41 ml / h,

$V_{C_6H_{11}OH}$ = 0.9 ml / h,

1 - conversion of $C_6H_{11}OH$; 2 – cyclohexene; 3 - 1, 2 cyclohexanediol; 4 - 1,3 cyclohexadiene; 5 - other oxygen-containing compounds; 6 - O_2



This mechanism is in good agreement with the fact that cyclohexanone is formed precisely through the use of the most concentrated hydrogen peroxide (30% or more) and at a lower temperature (150-180°C) (Fig. 2).

The conclusions above give us opportunity to present a scheme for conversion of cyclohexane on biomimetics with H_2O_2 into cyclohexanol, cyclohexanone and cyclohexene.

References

1. Aghamammadova S., Nagieva I., Gasanova L., Nagiev T. Coherent-Synchronized Biomimetic Monooxidation of Cyclohexane by Hydrogen Peroxide. *Russian Journal of Physical Chemistry A*, 2018, vol. 92, No. 12, pp. 2455–2463
2. Kustov L.M., Beletskaya I.P. “Green Chemistry”- a new thinking. *Russian Chemical Journal*. 2004, vol. XLVIII, no. 06. pp. 3-12.
3. Nagiev T.M. Chemical Conjugation. Moscow: Nauka Publ. 1989, 216 p. (In Russian).
4. Nagiev T.M. Coherent Synchronized Oxidation Reactions by Hydrogen Peroxide. Amsterdam: Elsevier. 2007, 325 p.
5. Nagiev T.M. Interaction of Synchronous Reactions in Chemistry and Biology. Baku: Elm Publ. 2001, 404 p. (In Azerbaijan).
6. Nagiev T.M. Coherent view of synchronous reactions. Baku: Sharq-Qarb Publ. 2018, 216 p. (In Azerbaijan).
7. Nagiev T., Gasanova L., Mustafaeva Ch. et.al. Selective Biomimetic Oxidation of Ethanol by Hydrogen Peroxide on Immobilized Ironporphyrin Catalysts. *Russian Journal of Physical Chemistry*. 2005, vol. 79, no. 3, pp. 382-388.
8. Nasirova U.V., Gasanova L.M., Nagiev T.M. The Monooxidation of Ethylene with Hydrogen Peroxide on the per-FTPhPFe^{3+}OH/Al$_2$O$_3$ Biomimetic. *Russian Journal of Physical Chemistry A*, 2010, vol. 84, no. 6, pp. 941-945.
9. Nagiev T., Gasanova L., Nagieva I., Nasirova U. Kinetics and Mechanism of Coherent Synchronized Ethylene Monooxidation by Hydrogen Peroxide on a Biomimetic Catalyst, per-FTPhPFe^{3+}OH/Al$_2$O$_3$. *Journal of Material Science and Engineering*, 2012, vol. 2, no. 4, pp. 306-312.
10. Nesmeyanov A.N., Nesmeyanov N.A. The beginning of organic chemistry 1. Moscow: Khimiya Publ., 1969, 664 p. (In Russian).
11. Aghamammadova S., Nagieva I., Gasanova L., Nagiev T. Catalytic monooxidation of cyclohexane by hydrogen peroxide in the gas phase. *Reaction Kinetics, Mechanisms and Catalysis.* 2019, vol. 126, issue 2, pp. 701–715.

TSİKLOHEKSANIN per-FTPhPFe^{3+}OH/Al$_2$O$_3$ ÜZƏRİNDƏ “YAŞIL OKSİDLƏŞDİRİCİ” HİDROGEN PEROKSİDLƏ OKSİDLƏŞMƏSİ MEXANİZMİNİN XÜSUSİYYƏTLƏRİ

S.Ə. Ağaməmmədova

AMEA-nın akad. M.Nağıyev adına Kataliz və Qeyri-üzvi Kimya İnstitutu,
H. Cavid pr.113, AZ 1143, Bakı, Azərbaycan
e-mail: aghamammadova@yahoo.com

per-FTPhPFe^{3+}OH/Al$_2$O$_3$ heterogen biomimetik katalizatoru üzərində tsikloheksanın hidrogen peroksidlə qaz fazada koherent-sinxronlaşdırılmış oksidləşməsi prosesinin məhsulları tsikloheksanol, tsikloheksanon və tsikloheksendən ibarətdir. Tsikloheksanın tsikloheksanona və tsikloheksenə çevrilmə yollarının aydınlaşdırılmasına yönəlmiş təcrübi tədqiqatlar tsikloheksanon və tsikloheksenin alınması mexanizmlərini müəyyənləşdirməyə imkan verdi, belə ki, tsikloheksanın tsikloheksanona çevrilməsi tsikloheksanolun əmələ gəlməsi ilə getmir, tsikloheksen isə tsikloheksanolun dehidratlaşması ilə əmələ gəlir. Tsikloheksanonun əmələ gəlməsi mexanizmi intermediatın (ImtOOH) tsikloheksanla qarşılıqlı təsiri nəticəsində yarananaralıq biomimetik-substrat kompleksin Imt-O-C$_6$H$_{11}$ yaranması ilə ifadə edilir.

Açar sözlər: *hidrogen peroksid, tsikloheksan, oksidləşmə, biomimetik katalizatorlar, tsikloheksanon, tsikloheksanol.*

ОСОБЕННОСТИ МЕХАНИЗМА ОКИСЛЕНИЯ ЦИКЛОГЕКСАНА “ЗЕЛЕНЫМ ОКИСЛИТЕЛЕМ” ПЕРОКСИДОМ ВОДОРОДА НА per-FTPhPFe^{3+}OH/Al_2O_3

С.А. Агамамедова

Институт Катализа и Неорганической Химии имени акад. М.Нагиева
Национальной АН Азербайджана,
пр. Г.Джавида 113, AZ1143, Баку, Азербайджан
e-mail: aghamammadova@yahoo.com

В процессе газофазного когерентно-синхронизированного окисления циклогексана пероксидом водорода в присутствии гетерогенного биомиметического катализатора per-FTPhPFe^{3+}OH/Al_2O_3 продуктами реакции являлись циклогексанол, циклогексанон и циклогексен. Экспериментальное исследование, проведенное с целью уточнения маршрутов превращения циклогексана в циклогексанон и циклогексен дало возможность определить механизмы получения циклогексанона и циклогексена, в которых показано, что превращение циклогексана в циклогексанон не происходит через образования циклогексанола, а образование циклогексена происходит путем дегидратации циклогексанола. Механизм образования циклогексанона выражается через образование промежуточного биомиметико - субстратного комплекса Imt-O-C_6H_{11}, который образуется при взаимодействии интермедиата (ImtOOH) с циклогексаном.

Ключевые слова: *пероксид водорода, циклогексан, окисление, биомиметические катализаторы, циклогексанон, циклогексанол.*