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RESEARCH ARTICLE

Epoxidation of cyclohexene with cyclohexyl hydroperoxide

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Abstract

Objectives. *To investigate the regularities of the process of joint production of epoxycyclohexane, cyclohexanol, and cyclohexanone using the cyclohexene epoxidation reaction with cyclohexyl hydroperoxide in the presence of an ammonium paramolybdate catalyst, representing an alternative to the method of cyclohexanol and cyclohexanone synthesis by alkaline catalytic decomposition of cyclohexyl hydroperoxide.*
Methods. *The qualitative and quantitative analysis of the obtained intermediate and target compounds was determined using modern physicochemical research methods: gas–liquid chromatography using the Chromatec-Crystal 5000.2 hardware and software complex with a flame ionization detector and infrared spectroscopy on an RX-1 infrared Fourier spectrometer. The content of hydroperoxide in the oxidation products was determined using iodometric titration, while the carboxylic acid content was determined by the titrimetric method based on the neutralization reaction.*
Results. *The presented method for obtaining cyclohexanol and cyclohexanone together with epoxycyclohexane by the reaction of cyclohexene epoxidation with cyclohexyl hydroperoxide containing cyclohexane in the products of high-temperature liquid-phase*

oxidation is experimentally substantiated. The influence of various technological parameters on the process of liquid-phase oxidation of cyclohexane to hydroperoxide is described. The conditions for carrying out this reaction are determined to ensure the achievement of a content of cyclohexyl hydroperoxide of 1.5 wt % in the products of oxidation. The regularities of the epoxidation reaction of the synthesized cyclohexyl hydroperoxide with cyclohexene in the presence of an ammonium paramolybdate catalyst are analyzed.

Conclusions. *Epoxidation of cyclohexene with cyclohexyl hydroperoxide produced epoxycyclohexane at a yield of 80–90% and a conversion of cyclohexane hydroperoxide of 85%.*

Keywords: *cyclohexene, cyclohexane, cyclohexyl hydroperoxide, cyclohexanone, cyclohexanol, liquid phase oxidation, epoxidation*

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НАУЧНАЯ СТАТЬЯ

Эпоксидирование циклогексена гидропероксидом циклогексила

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Аннотация

Цели. *Исследование закономерностей процесса совместного получения эпоксициклогексана, циклогексанола, циклогексанона реакцией эпоксидирования циклогексена гидропероксидом циклогексила в присутствии катализатора — парамолибдата аммония. Разрабатываемый процесс является альтернативой способу синтеза циклогексанола и циклогексанона щелочно-каталитическим разложением гидропероксида циклогексила.*

Методы. *Определение качественного и количественного анализа полученных промежуточных и целевых соединений осуществлялось с применением газожидкостной хроматографии на аппаратно-программном комплексе «Хроматек-Кристалл 5000.2» с пламенно-ионизационным детектором, инфракрасной спектроскопией на приборе*

ИК Фурье RX-1. Содержание гидропероксида в продуктах окисления проводилось с использованием йодометрического титрования, а содержание карбоновых кислот — титриметрическим методом на основе реакции нейтрализации.

Результаты. *Экспериментально обоснован метод получения циклогексанола и циклогексанона совместно с эпоксициклогексаном реакцией эпоксидирования циклогексена гидропероксидом циклогексила, содержащимся в продуктах высокотемпературного жидкофазного окисления циклогексана. Исследовано влияние различных технологических параметров на процесс жидкофазного окисления циклогексана до гидропероксида. Определены условия проведения данной реакции, обеспечивающие достижение содержания гидропероксида циклогексила 1.5 мас. % в продуктах окисления. Изучены закономерности реакции эпоксидирования синтезированного гидропероксида циклогексила с циклогексеном в присутствии парамолибдата аммония в качестве катализатора.*

Выводы. *Эпоксидированием циклогексена гидропероксидом циклогексила получен эпоксициклогексан с выходом 80–90% при конверсии гидропероксида циклогексана 85%.*

Ключевые слова: *циклогексен, циклогексан, гидропероксид циклогексила, циклогексанон, циклогексанол, жидкофазное окисление, эпоксидирование*

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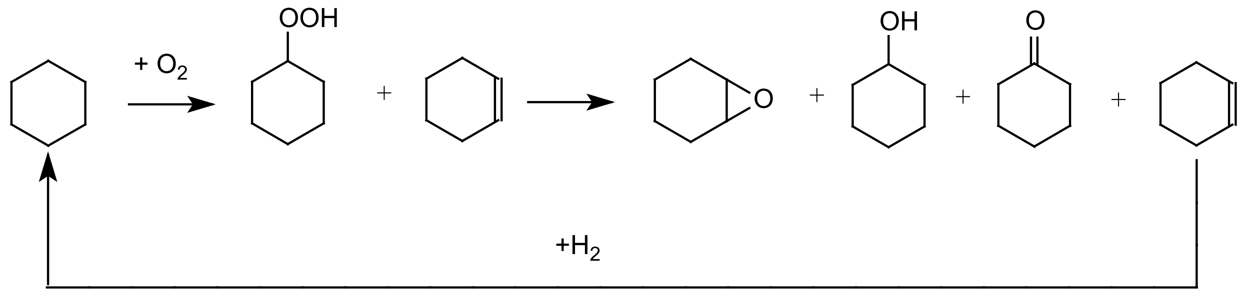
INTRODUCTION

The selective oxidation of cyclohexane to cyclohexanone and cyclohexanol is a key stage in the process of producing nyolone-6 and nylon-6,6 polyamides, whose global production of which reaches more than 6 mln t/year.

Two main methods are implemented for the industrial production of cyclohexanol and cyclohexanone both in Russia and abroad. A one-step method for the synthesis of these compounds is based on the catalytic liquid-phase oxidation of cyclohexane with air oxygen at 150–170°C to a cyclohexane conversion of 5–7% and a selectivity for cyclohexanone and cyclohexanol formation of 70–75% in the presence of cobalt-containing catalysts [1]. A two-stage method for the production of cyclohexanone and cyclohexanol includes autocatalytic liquid-phase oxidation of cyclohexane to cyclohexyl hydroperoxide containing 3–5 wt % and subsequent homogeneous catalytic decomposition of cyclohexyl hydroperoxide to the target products in an alkaline medium in the presence of cobalt salts [2]. The scientific basis of the chemistry and technology of the latter method for producing cyclohexanone and cyclohexanol were developed at the Research and Design Institute of Nitrogen Industry and Products of Organic Synthesis (*GIAP*, Russia) by V.V. Lipes and his colleagues during the 1980s [3–4].

A distinctive feature of the two-stage process is the higher selectivity of target product formation (97–99%), achieving a 94–96% conversion of cyclohexyl hydroperoxide. However, among the significant disadvantages of this cyclohexane oxidation method are included the formation of a large amount of alkaline waste as a result of neutralization of acids contained in the oxidation products, as well as the irreversible loss of oxygen (up to 50%) contained in the hydroperoxide fragment.

In order to improve the economic and technological efficiency of this approach for cyclohexanol and cyclohexanone production the alkali-catalytic cleavage of cyclohexyl hydroperoxide can be replaced with the use of hydroperoxide to epoxidate olefins, among which cyclohexene is of greatest interest (Scheme).



Scheme. Reaction of cyclohexene epoxidation with hydroperoxide.

Epoxycyclohexane formed along with cyclohexanol and cyclohexanone as a result of the epoxidation reaction is used in the production of epoxy resins and photoreactive polymers, pesticide acaricides, surfactants, and rubber additives [5–7]. A promising use of cyclohexane epoxide lies in its enantioselective transformation into chiral 1,2-aminocyclohexanol or 1,2-diaminocyclohexane, representing chemical building blocks for the preparation of natural and synthetic biologically active molecules, including amino acids [8, 9]. The epoxide can be used as such or converted into cyclohexanol or cyclohexanone for subsequent processing into adipic acid or ε-caprolactam [10–12]. Unreacted cyclohexene following hydrogenation can be sent for oxidation.

The aim of the present work is to study the regularities of cyclohexene epoxidation with cyclohexyl hydroperoxide.

MATERIALS AND METHODS

The following reagents were used in this study: cyclohexanol (reagent grade, TU-2632-185-44493179-2017) and cyclohexane (reagent grade, TU 2631-204-44493179-2016, *EKOS-1*, Russia), sulfuric acid (reagent grade, GOST 4204-77[1], *Sigma Tek*, Russia), ammonium molybdate tetrahydrate (reagent grade, GOST 3765-78[2], *Khimsintez*, Russia), propylene glycol (TU 2632-146-44493179-11, *EKOS-1*, Russia), acetic acid (reagent grade, GOST 61-75[3]) and potassium oxide (reagent grade, GOST 4232-74[4], *Spektr Khim*, Russia), sodium hyposulfite (analytical grade, GOST 27068-86[5], *Uralkhiminvest*, Russia), sodium hydroxide (analytical grade, GOST 4328-77[6], *Kaustik*, Russia), phenolphthalein (analytical grade, TU 6-09-5360-88, *Spektr Khim*, Russia).

The main method for analyzing the reaction mass was gas-liquid chromatography (GLC) carried out on a Chromatec-Crystal 5000.2 chromatograph (*Chromatec*, Russia) with a flame ionization detector. A 30-m capillary column SK-5 having a diameter of 0.32 mm was filled with 5% phenyl/95% dimethylpolysiloxane. Nitrogen was used as a carrier gas at a flow rate 2 cm^3/min. The programmed temperature rise was from 80 to 200°C at a rate of 8°C/min.

The identification of the obtained compounds was carried out by infrared (IR) spectroscopy on a Spectrum RX-1 Fourier transform IR spectrometer (*PerkinElmer*, USA). Mathematical processing of the spectra was carried out using the IBM Spectrum Scale, v.5.0.1 program provided by *PerkinElmer*. Spectra were recorded in the range of 4000–400 cm^{-1} in the form of a microlayer between potassium bromide glasses and in a potassium bromide cuvette with a layer thickness $d = 0.0011$.

The hydroperoxide content in the oxidation products was determined by the iodometric titration method [13] based on hydroperoxide reduction with potassium iodide in an acidic medium. The amount of iodine released as a result of the reaction was titrated with a solution of sodium thiosulfate.

The content of carboxylic acids formed along with hydroperoxide in the process of cyclohexane oxidation was determined by the titrimetric method

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[1] GOST 4204-77. State Standard of the USSR. Reagents. Sulphuric acid. Specifications. Moscow: Standartinform; 2006.

[2] GOST 3765-78. State Standard of the USSR. Reagents. Ammonium molybdate acid. Specifications. Moscow: IPK Izdatelstvo standartov; 1998.

[3] GOST 61-75. Interstate Standard. Reagents. Acetic acid. Specifications. Moscow: Standartinform; 2006.

[4] GOST 4232-74. Interstate Standard. Reagents. Potassium iodide. Specifications. Moscow: Standartinform; 2006.

[5] GOST 27068-86. Interstate Standard. Reagents. Sodium thiosulphate, 5-aqueous. Specifications. Moscow: IPK Izdatelstvo standartov; 1998.

[6] GOST 4328-77. Interstate standard. Reagents. Sodium hydroxide. Specifications. Moscow: IPK Izdatelstvo standartov; 1978.

based on the neutralization of an aqueous extract obtained from a certain organic layer mass using a solution of sodium hydroxide in the presence of the indicator phenolphthalein according to the method described by *KuibyshevAzot*. Russia.

EXPERIMENTAL

Cyclohexene was obtained by cyclohexanol dehydration in the presence of concentrated sulfuric acid at 110–120°C for 1.5 h. The process was carried out in a Wurtz flask placed in a glycerol bath and equipped with a Weigel–Liebig refrigerator. Water and cyclohexene formed during the reaction were evaporated, condensed in a direct refrigerator, and collected in the receiver. The target product was isolated from the reaction mass by vacuum rectification at a temperature of 83–85°C and a residual pressure of 0.8–0.9 atm. The yield of cyclohexene was about 80%; its structure was confirmed by GLC and IR spectroscopy. The IR spectrum of the synthesized cyclohexene displays the characteristic bands of stretching vibrations of C–H bonds with bands at 3022 and 2925 cm^{-1}. The presence of a C=C bond in the structure is confirmed by the band at 1652.93 cm^{-1}. Deformation vibrations of the $–CH_2$ bond are characterized by bands at 1446.15 and 1437.73 cm^{-1}.

Liquid-phase oxidation of cyclohexane to hydroperoxide with air oxygen at a system pressure of 25 atm was carried out at 160–170°C in a steel reactor set up for the oxidation of liquefied hydrocarbon gases (Fig. 1) according to the method described in [14, 15] while simulating the conditions of high-temperature oxidation of cyclohexane by *KuibyshevAzot*.

The approximately 1.5 wt % cyclohexyl hydroperoxide obtained in the oxidation products, which was concentrated by vacuum rectification at a temperature of 65–70°C and a residual pressure of 0.15–0.2 atm to 5 wt %, was used for subsequent research purposes.

Cyclohexene epoxidation with cyclohexyl hydroperoxide was carried out in a closed-flow installation (Fig. 2) made available at the Department of General and Physical Chemistry of Yaroslavl State Technical University. A mixture containing calculated amounts of fortified cyclohexane oxidate with a hydroperoxide content of 5 wt % was loaded into a glass reactor having a capacity of 10 cm^3 along with cyclohexene and the catalyst. Air was supplied at atmospheric pressure. The process was carried out at a constant temperature and continuous stirring [16].

Ammonium paramolybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ dissolved in propylene glycol was used as a catalyst for cyclohexene epoxidation with cyclohexyl hydroperoxide. The process was carried out according to the method described in [17] in an electrically-heated, round-bottomed, four-neck 150-mL flask equipped with a reflux condenser, a thermometer, a stirrer, and a bubbler for purging the reaction mixture with air.

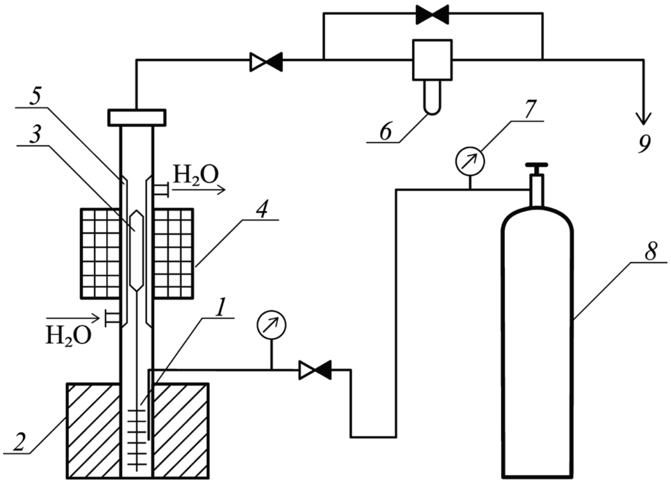

Fig. 1. Scheme of a setup for the oxidation of liquefied hydrocarbon gases [14, 15]: (*1*) autoclave; (*2*) electric furnace; (*3*) magnetic stirrer; (*4*) electromagnet; (*5*) fridge; (*6*) rheometer; (*7*) reducer; (*8*) compressed air cylinder; (*9*) air discharge; ►◄ adjusting valve.

RESULTS AND DISCUSSION

Although information concerning the regularities of olefins epoxidation with hydroperoxides is abundant, there is practically no data relating to the process of cyclohexene epoxidation with cyclohexyl hydroperoxide in the scientific and technical literature. However, the synthesis of cyclohexanol and cyclohexanone together with epoxycyclohexane by epoxidizing cyclohexene with cyclohexyl hydroperoxide is described at a conversion of the latter of 60–65% on a heterogeneous Ti/Si catalyst at 80°C [18, 19]. The limited number of scientific studies and publications on the above problem is primarily due to the difficulties of obtaining cyclohexane hydroperoxide, as well as its extremely low stability during storage and transportation.

The study of the patterns of cyclohexene epoxidation using cyclohexyl hydroperoxide was preceded by a study of the conditions for high-temperature oxidation of cyclohexane to cyclohexyl hydroperoxide, as well as its concentration and production in larger quantities. This problem was

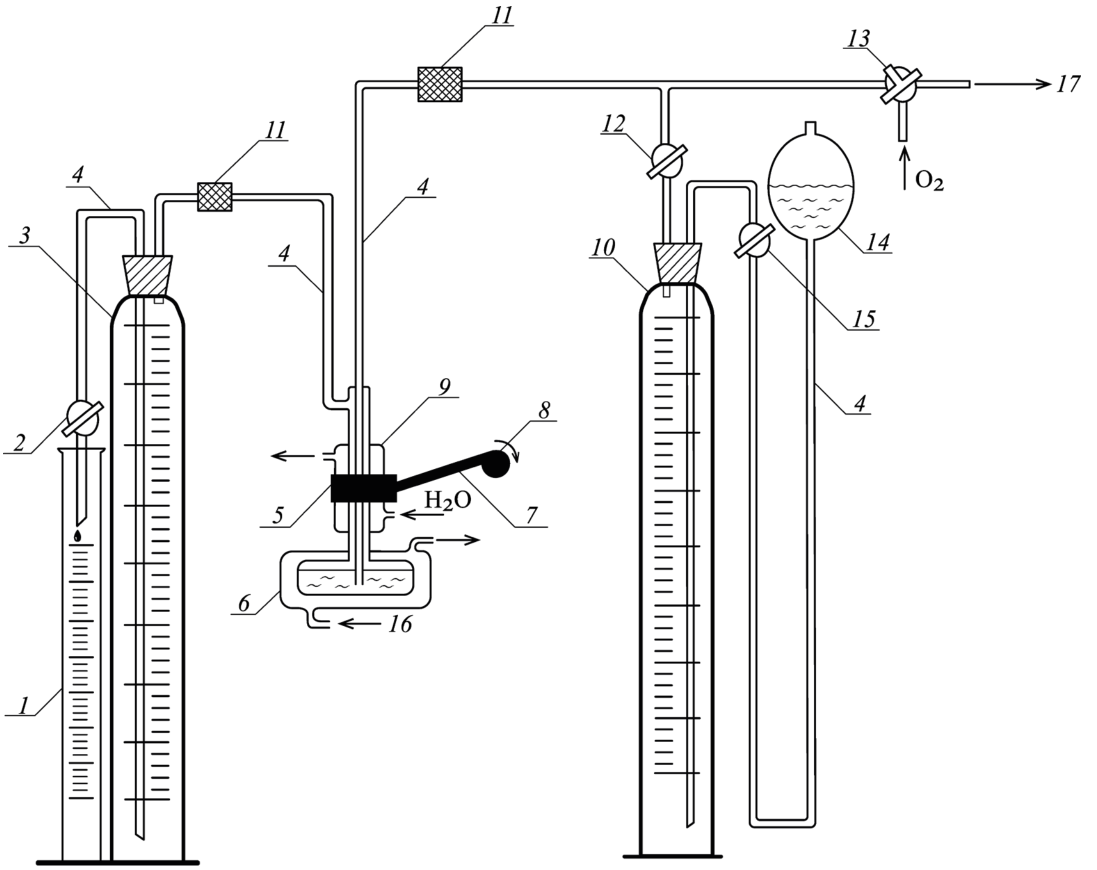

Fig. 2. Scheme of the setup for cyclohexene epoxidation with cyclohexyl hydroperoxide [16]: (*1*) measuring cylinder; (*2*), (*12*), (*15*) valves; (*3*), (*10*) gas burettes; (*4*) connecting hose; (*5*) reactor holder; (*6*) reactor; (*7*) connecting rod; (*8*) electric motor pulley; (*9*) fridge; (*11*) calcium chloride tube; (*13*) three-way cock; (*14*) pressure bottle; (*16*) thermostat; (*17*) vacuum setup.

solved by carrying out liquid-phase oxidation of cyclohexane under conditions as close as possible to those used at *KuibyshevAzot*.

A study of the influence of temperature and reaction duration on cyclohexyl hydroperoxide formation (Table 1) showed that at a temperature of 160°C, an increase in the process duration from 20 to 40 min increases the content of cyclohexyl hydroperoxide slightly; in this case, the content of carboxylic acids formed along with the target products increases by a factor of six. A subsequent increase in temperature leads to a significant decrease in the process selectivity due to the formation of a large quantity of carboxylic acids.

Thus, the possibility of achieving a hydroperoxide content in the oxidate of 1.5 wt % with a minimum content of carboxylic acids at a temperature of 160°C, a pressure in the system of 25 atm and a reaction duration of 20 min is demonstrated. This is consistent with the indicators of the oxidation process at *KuibyshevAzot*. After increasing the cyclohexyl hydroperoxide content in the oxidate to 5 wt % according to the method given in the Experimental section, the product was used for cyclohexene epoxidation. In [18], cyclohexene epoxidation was carried out using cyclohexyl hydroperoxide isolated from the products of cyclohexane catalytic oxidation using a NaOH solution.

In order to determine the most favorable conditions for carrying out the epoxidation reaction, the influence of the molar ratio of reagents, catalyst concentration, and temperature on the yield of target products and hydroperoxide conversion was studied. The results obtained are presented in Figs. 3 and 4 and in Tables 2 and 3.

One of the factors that significantly influences both the yield of target products and the rate of hydroperoxide conversion is the molar ratio of cyclohexyl hydroperoxide and cyclohexene (Fig. 1). Changing this ratio from 1:1 to 3:1 increases the yield of epoxycyclohexane with respect to reacted hydroperoxide from 30–35% to 75–80%. In this case, the selectivity of cyclohexanol and cyclohexanone formation increases to 99.5%.

Table 1. Influence of various parameters on cyclohexane oxidation. Pressure is 25 atm

Temperature, °C	Reaction time, min	Concentration, wt %	
		Cyclohexyl hydroperoxide	Carboxylic acids
160	20	1.5	0.06
	30	1.6	0.27
	40	1.7	0.36
170	20	1.5	0.14

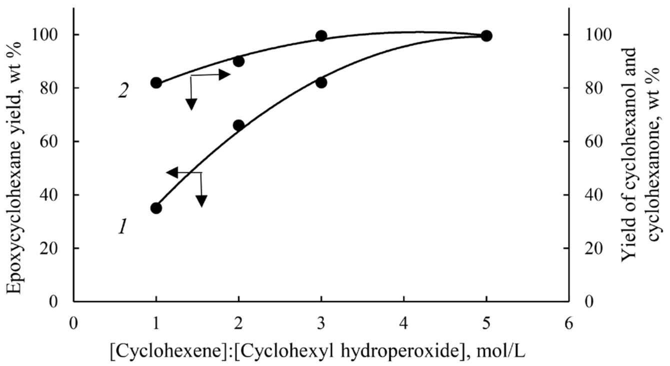

Fig. 3. Influence of the molar ratio of cyclohexyl hydroperoxide and cyclohexene on cyclohexene epoxidation with cyclohexyl hydroperoxide at a temperature of 90°C and a catalyst concentration of 0.00013 g/atom of Mo per 1 g of hydroperoxide: (*1*) yield of epoxycyclohexane; (*2*) yield of cyclohexanol and cyclohexanone.

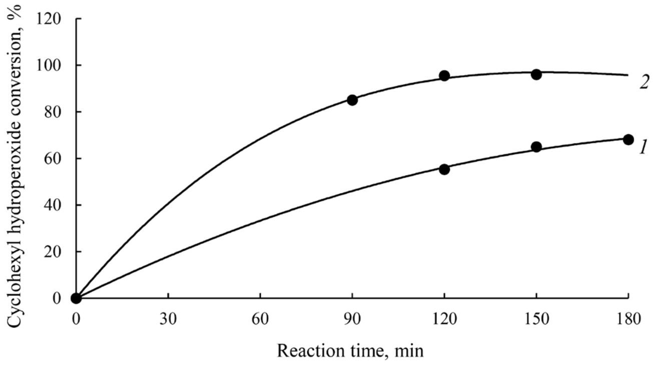

Fig. 4. Influence of temperature on cyclohexene epoxidation with cyclohexyl hydroperoxide. Cyclohexyl hydroperoxide/cyclohexene ratio is 1:3, the catalyst concentration is 0.0005 g/Mo atom per 1 g of hydroperoxide: (*1*) 80°C; (*2*) 90°C.

From analyzing the influence of temperature and cyclohexene epoxidation duration (Table 2) it was shown that complete conversion of cyclohexyl hydroperoxide cannot be achieved at 80°C even after 3 h of reaction. In addition, a low yield of epoxycyclohexane is observed. By increasing the temperature to 90°C, the process was significantly intensified due to the increased conversion of cyclohexyl hydroperoxide from 65% to 95%. Under these conditions, no boiling of the reaction mass was observed. Conversely, lowering the temperature to 70°C significantly reduces the reaction rate. Thus, the most favorable temperature is 90°C.

Reducing the catalyst concentration from 0.0005 to 0.00003 g/Mo atom per 1 g of hydroperoxide results in a decrease in the conversion of cyclohexyl hydroperoxide and in the yield of epoxycyclohexane (Table 3). Thus, a yield of epoxycyclohexane of about 82% is achieved with an ammonium paramolybdate content of 0.00013 g/Mo atom per 1 g of hydroperoxide. Further reduction of the catalyst concentration is impractical due to a decrease in the yield of epoxycyclohexane, while increasing catalyst concentration above 0.0005 g/Mo atom per 1 g of hydroperoxide is not economically feasible.

Based on the obtained experimental data, the following conditions can be recommended for cyclohexene epoxidation with cyclohexyl hydroperoxide: temperature is 90°C; reaction duration is 90 min; ammonium paramolybdate content is 0.00013 g/Mo atom per 1 g of hydroperoxide. Under these conditions, cyclohexyl hydroperoxide conversion is 85%, while the yield of epoxycyclohexane is about 82%, and the yield of cyclohexanol and cyclohexanone is 99.5%.

Table 2. Influence of various parameters on cyclohexene epoxidation with cyclohexyl hydroperoxide. Cyclohexyl hydroperoxide/cyclohexene ratio is 1:3. The catalyst concentration is 0.0005 g/Mo atom per 1 g hydroperoxide

Temperature, °C	Reaction time, min	Cyclohexyl hydroperoxide conversion, %	Yield per reacted cyclohexyl hydroperoxide, %		Cyclohexanol/cyclohexanone molar ratio
			Cyclohexanone + cyclohexanol	Epoxycyclohexane	
80	120	55.3	96.0	35.0	4:1
	150	65.0	99.0	38.0	3:1
	180	68.0	99.2	45.0	5:1
90	60	33.0	98.0	75.0	4:1
	90	94.5	99.1	80.0	4:1
	120	95.5	99.3	78.0	4:1
	150	96.0	99.4	75.0	2:1

Table 3. Influence of catalyst concentration on cyclohexene epoxidation with cyclohexyl hydroperoxide. Cyclohexyl hydroperoxide/cyclohexene ratio is 1:3, temperature is 90°C, reaction time is 90 min

Catalyst concentration, g/Mo atom per 1 g of hydroperoxide	Cyclohexyl hydroperoxide conversion, %	Yield per reacted cyclohexyl hydroperoxide, %		Cyclohexanol/ cyclohexanone molar ratio
		Cyclohexanol + cyclohexanone	Epoxycyclohexane	
0.00003	77.0	76.2	65.0	1:1
0.00013	85.0	99.5	82.1	4:1
0.00025	87.0	99.4	99.5	4:1
0.00050	95.0	94.5	99.1	4:1

CONCLUSIONS

The possibility of producing epoxycyclohexane together with cyclohexanol and cyclohexanone by epoxidizing cyclohexene with cyclohexyl hydroperoxide contained in the products of high-temperature, liquid-phase oxidation of cyclohexane as an alternative to the process of producing cyclohexanol and cyclohexanone by alkaline-catalytic decomposition of cyclohexyl hydroperoxide is experimentally substantiated.

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Authors' contributions

E.A. Kurganova – research concept, design of the experiments, analysis of the results, writing the text of the manuscript;

A.S. Frolov – research concept, data processing, writing the text of the manuscript;

S.A. Kanaev – analysis of the results;

G.N. Koshel – research concept, analysis of the results, writing the text of the manuscript;

A.A. Petukhov – research concept, analysis of the results;

G.V. Rybina – analysis of the results;

V.V. Plakhtinskii – analysis of the results, writing the text of the manuscript;

V.S. Kabanova – conducting the experiments, writing the text of the manuscript;

A.A. Smurova – conducting the experiments, writing the text of the manuscript.

The authors declare no conflicts of interest.

REFERENCES

1. Lebedev N.N. *Khimiya i tekhnologiya osnovnogo organicheskogo i neftekhimicheskogo sinteza* (*Chemistry and Technology of Basic Organic and Petrochemical Synthesis*). Moscow: Al'yanS; 2013. 588 p. (in Russ.). ISBN 978-5-91872-035-6

2. Lipes V.V., Geberger F.A., Khar'kova T.V., Shafran M.I., Uspenskii V.B., Pravdivyi I.N., Bukseev V.V., Stepenyuk L.S., Polyukhovich I.D. *Method of Obtaining Cyclohexanone and Cyclohexanol*: USSR Pat. RU1641804. Publ. 15.04.1991 (in Russ.).

3. Furman M.S., Lipes V.V., Goltyaeva N.A. Investigation of the process of liquid-phase high-temperature oxidation of cyclohexane. *Khimiya i tekhnologiya produktov organicheskogo sinteza = Chemistry and Technology of Organic Synthesis Products*. 1966;17(1):21–30 (in Russ.).

4. Furman M.S., Arrest-Yakubovich I.A., Lipes V.V. Thermal and alkaline decomposition of cyclohexane hydroperoxide in oxidants obtained by high-temperature oxidation of cyclohexane. *Khimiya i tekhnologiya produktov organicheskogo sinteza = Chemistry and Technology of Organic Synthesis Products*. 1974;27:46–56 (in Russ.).

СПИСОК ЛИТЕРАТУРЫ

1. Лебедев Н.Н. *Химия и технология основного органического и нефтехимического синтеза*. М.: АльянС; 2013. 588 с. ISBN 978-5-91872-035-6

2. Липес В.В., Гебергер Ф.А., Харькова Т.В., Шафран М.И., Успенский В.Б., Правдивый И.Н., Буксеев В.В., Степенюк Л.С., Полюхович И.Д. *Способ получения циклогексанона и циклогексанола*: авторское свидетельство 1641804 СССР. Заявка № 4655478/04; заявл. 29.12.1988; опубл. 15.04.1991. Бюл. № 14.

3. Фурман М.С., Липес В.В., Гольтяева Н.А. Исследование процесса жидкофазного высокотемпературного окисления циклогексана. *Химия и технология продуктов органического синтеза*. 1966;17(1):21–30.

4. Фурман М.С., Арест-Якубович И.А., Липес В.В. Термическое и щелочное разложение гидропероксида циклогексана в оксидатах, полученных высокотемпературным окислением циклогексана. *Химия и технология продуктов органического синтеза.* 1974;27:46–56.

5. Wittcoff H.A., Reuben B.G., Plotkin J.S. *Industrial Organic Chemicals*. Hoboken, New Jersey: John Wiley & Sons; 2004. 662 p.

5. Wittcoff H.A., Reuben B.G., Plotkin J.S. *Industrial Organic Chemicals*. Hoboken, New Jersey: John Wiley & Sons; 2004. 662 p.

6. Kotelnikova T.S., Voronina S.G., Puchkov S.V., Perkel A.L. Assessment of reactionary of cyclohexene oxide in relation to *tert*-butylperoxy radical. *Vestnik Kuzbasskogo gosudarstvennogo tekhnicheskogo universiteta = Bulletin of the Kuzbass State Technical University*. 2013;5(99):4–9 (in Russ.).

7. Yahiaouia A., Belbachir M., Soutif J.C., Fontaine L. Synthesis and structural analyses of poly (1, 2-cyclohexene oxide) over solid acid catalyst. *Mater. Lett*. 2005;59:759–767. https://doi.org/10.1016/j.matlet.2004.11.017

8. Seo T., Tsuji J. *Process for Producing Propylene Oxide*: Pat. US 6646139. Publ. 11.11.2003.

9. Fischer R., Weitz H.-M., Rieber N., Boehm H. *Process for the Preparation of Oxiranes*: Pat. EU 0129814. Publ.16.06.1984.

10. Accrombessi G.C., Geneste P., Olive J.-L., Pavia A.A. Mechanism of the liquid-phase catalytic hydrogenolysis on palladium/carbon of cyclohexene epoxides. *J. Org. Chem.* 1980;45(21):4139–4143. https://doi.org/10.1021/jo01309a014

11. Dahlhoff G., Barsnick U., Hölderich W.F. Use of MCM-22 as catalyst for the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam. *Appl. Catal. A: General.* 2001;210(1–2):83–95. https://doi.org/10.1016/S0926-860X(00)00789-4

12. Fasi A., Palinko I. Transformations of cyclohexene oxide over silica-supported Cu, Pd, and Rh catalysts in H_2/D_2 atmosphere. *J. Catal*. 1999;181(1):28–36. https://doi.org/10.1006/jcat.1998.2284

13. Antonovskii V.L., Buzlanova M.M. *Analiticheskaya khimiya organicheskikh peroksidnykh soedinenii* (*Analytical Chemistry of Organic Peroxidic Compounds*). Moscow: Khimiya; 1978. 309 p. (in Russ.).

14. Frolov A.S., Kurganova E.A., Yarkina E.M., Lebedeva N.V., Koshel G.N., Kalenova A.S. Intensification of the cyclohexane liquid phase oxidation process. *Tonk. Khim. Tekhnol. = Fine Chem. Technol*. 2018;13(4):50–57 (in Russ.). https://doi.org/10.32362/2410-6593-2018-13-4-50-57

15. Kurganova E.A., Frolov A.S., Koshel G.N., Kabanova V.S. The reaction of cyclohexylbenzene oxidation in the presence of solvents. *Ot khimii k tekhnologii shag za shagom = From Chemistry Towards Technology Step-By-Step*. 2022;3(1):88–94 (in Russ.). https://doi.org/10.52957/27821900_2022_01_88

16. Frolov A.S., Kurganova E.A., Koshel' G.N. Nesterova T.N. Aerobic Oxidation of 2-isopropyl-1,4-dimethylbenzene to tertiary hydroperoxide. *Eur. J. Anal. Appl. Chem*. 2015;(1):16–22. https://doi.org/10.20534/EJAAC-15-1-16-22

17. Puchkova T.L., Nasrtdinova R.R., Pisareva M.L. The use of a glycol solution of molybdenum as a catalyst in the process of epoxidation of propylene with ethylbenzene hydroperoxide. *Vestnik tekhnologicheskogo universiteta = Herald of Technological University*. 2015;18(24):27–29 (in Russ.).

18. Hereijgers B.P.C., Parton R.F., Weckhuysen B.M. Cyclohexene Epoxidation with Cyclohexyl Hydroperoxide: A Catalytic Route to Largely Increase Oxygenate Yield from Cyclohexane Oxidation. *ACS Catal*. 2011;1(10):1183–1192. https://doi.org/10.1021/cs200354c

19. Hereijgers B.P.C., Parton R.F., Weckhuysen B.M. Mechanistic insights in the olefin epoxidation with cyclohexyl hydroperoxide. *Catal. Sci. Technol*. 2012;2(5):951–960. https://doi.org/10.1039/C2CY00455K

6. Котельникова Т.С., Воронина С.Г., Пучков С.В., Перкель А.Л. Оценка реакционной способности циклогексеноксида по отношению к *трет*-бутилпероксирадикалу. *Вестник Кузбасского государственного технического университета.* 2013;5(99):4–9.

7. Yahiaouia A., Belbachir M., Soutif J.C., Fontaine L. Synthesis and structural analyses of poly (1, 2-cyclohexene oxide) over solid acid catalyst. *Mater. Lett*. 2005;59:759–767. https://doi.org/10.1016/j.matlet.2004.11.017

8. Seo T., Tsuji J. *Process for Producing Propylene Oxide*: Pat. US 6646139. Publ. 11.11.2003.

9. Fischer R., Weitz H.-M., Rieber N., Boehm H. *Process for the Preparation of Oxiranes*: Pat. EU 0129814. Publ.16.06.1984.

10. Accrombessi G.C., Geneste P., Olive J.-L., Pavia A.A. Mechanism of the liquid-phase catalytic hydrogenolysis on palladium/carbon of cyclohexene epoxides. *J. Org. Chem.* 1980;45(21):4139–4143. https://doi.org/10.1021/jo01309a014

11. Dahlhoff G., Barsnick U., Hölderich W.F. Use of MCM-22 as catalyst for the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam. *Appl. Catal. A: General.* 2001;210(1–2):83–95. https://doi.org/10.1016/S0926-860X(00)00789-4

12. Fasi A., Palinko I. Transformations of cyclohexene oxide over silica-supported Cu, Pd, and Rh catalysts in H_2/D_2 atmosphere. *J. Catal*. 1999;181(1):28–36. https://doi.org/10.1006/jcat.1998.2284

13. Антоновский В.Л., Бузланова М.М. *Аналитическая химия органических пероксидных соединений*. М.: Химия; 1978. 309 с.

14. Фролов А.С., Курганова Е.А., Яркина Е.М., Лебедева Н.В., Кошель Г.Н., Каленова А.С. Интенсификация процесса жидкофазного окисления циклогексана. *Тонкие химические технологии*. 2018;13(4):50–57. https://doi.org/10.32362/2410-6593-2018-13-4-50-57

15. Курганова Е.А., Фролов А.С., Кошель Г.Н., Кабанова В.С. Изучение реакции окисления циклогексилбензола в присутствии растворителей. *От химии к технологии шаг за шагом*. 2022;3(1):21–27. https://doi.org/10.52957/27821900_2022_01_21

16. Frolov A.S., Kurganova E.A., Koshel' G.N. Nesterova T.N. Aerobic Oxidation of 2-isopropyl-1,4-dimethylbenzene to tertiary hydroperoxide. *Eur. J. Anal. Appl. Chem*. 2015;(1):16–22. https://doi.org/10.20534/EJAAC-15-1-16-22

17. Пучкова Т.Л., Насртдинова Р.Р., Писарева М.Л. Использование гликолевого раствора молибдена в качестве катализатора в процессе эпоксидирования пропилена гидропероксидом этилбензола. *Вестник технологического университета*. 2015;18(24):27–29.

18. Hereijgers B.P.C., Parton R.F., Weckhuysen B.M. Cyclohexene Epoxidation with Cyclohexyl Hydroperoxide: A Catalytic Route to Largely Increase Oxygenate Yield from Cyclohexane Oxidation. *ACS Catal*. 2011;1(10):1183–1192. https://doi.org/10.1021/cs200354c

19. Hereijgers B.P.C., Parton R.F., Weckhuysen B.M. Weckhuysen. Mechanistic insights in the olefin epoxidation with cyclohexyl hydroperoxide. *Catal. Sci. Technol*. 2012;2(5):951–960. https://doi.org/10.1039/C2CY00455K

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