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Highly efficient catalytic system for liquid-phase oxidation of 1-chloro-*n*-hexadecane with atmospheric oxygen

Valentin N. Sapunov[1], **Yuriy L. Zotov**[2,✉], **Nguyen Thanh Tung**[2], **Yuriy V. Popov**[2], **Evgeniy V. Shishkin**[2]
[1] *Mendeleev University of Chemical Technology of Russia, Moscow, 125047 Russia*
[2] *Volgograd State Technical University, Volgograd, 400005 Russia*
✉ *Corresponding author, e-mail: ylzotov@mail.ru*

Abstract

Objectives. To develop a highly efficient catalytic system for the liquid-phase oxidation of long-chain mono-chlorinated alkanes by oxygen in air to a mixture of high-boiling chlorinated carboxylic acids, which can serve as raw materials for the production of multifunctional additives for polyvinyl chloride.

Methods. The liquid-phase oxidation of 1-chloro-*n*-hexadecane by oxygen in air in the presence of a two-component catalytic system of $St_2Co(OH)$ and *N*-hydroxyphthalimide (*N*-HPI) was investigated. The air flow rate during the oxidation of 1-chloro-*n*-hexadecane was controlled by a gas meter. Identification, composition, and content of the starting 1-chloro-*n*-hexadecane for conversion control were conducted using chromatographic-mass spectrometric analysis on an Agilent GC 7820A/MSD 5975 instrument. The structure of cobalt(III) hydroxystearate was confirmed by infrared spectroscopy.

Results. Investigation of a two-component catalytic system $St_2Co(OH)$–*N*-HPI in the oxidation reaction of 1-chloro-*n*-hexadecane by oxygen in air revealed that both components of the system participate in the formation of hydroperoxides. This accelerates their formation and contributes to high hydroperoxide content in the reaction mass. It was observed that $St_2Co(OH)$ in the two-component catalytic system accelerates the decomposition of hydroperoxides better than St_2Co in another two-component catalytic system previously studied, making it promising for application in the process. The oxides thus obtained can serve as raw materials for the production of multifunctional additives for polyvinyl chloride which could lead to improvements in the quality and properties of this material.

Conclusions. The investigation into the liquid-phase oxidation of 1-chloro-*n*-hexadecane by oxygen in air using the two-component catalytic system $St_2Co(OH)$–*N*-HPI has shown it to be more efficient compared to the two-component catalytic system St_2Co–*N*-HPI. The optimal concentration of the two-component catalytic system $St_2Co(OH)$–*N*-HPI in the reaction system for the liquid-phase oxidation of 1-chloro-*n*-hexadecane by oxygen in air has been determined to be 9 mol % of the raw material loading, with a molar ratio of components of 1 : 6. Such a catalytic system enables an acid number in the oxide of 42 mg KOH/g to be attained after 10 h of oxidation.

Keywords

1-chloro-*n*-hexadecane, liquid-phase catalytic oxidation, two-component catalytic system, cobalt hydroxystearate, *N*-hydroxyphthalimide, hydroperoxide, conversion, acid number, carboxylic acids

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НАУЧНАЯ СТАТЬЯ

Высокоэффективная каталитическая система для жидкофазного окисления 1-хлор-*н*-гексадекана кислородом воздуха

В.Н. Сапунов[1], Ю.Л. Зотов[2,✉], Нгуен Тхань Тунг[2], Ю.В. Попов[2], Е.В. Шишкин[2]

[1] *Российский химико-технологический университет им. Д.И. Менделеева, Москва, 125047 Россия*

[2] *Волгоградский государственный технический университет, Волгоград, 400005 Россия*

✉ *Автор для переписки, e-mail: ylzotov@mail.ru*

Аннотация

Цели. Разработка высокоэффективной каталитической системы для жидкофазного окисления длинноцепочечных монохлорированных алканов кислородом воздуха в смесь высококипящих хлорсодержащих карбоновых кислот, которые могут служить сырьем для получения многофункциональных добавок для поливинилхлорида.

Методы. Исследование жидкофазного окисления 1-хлор-*н*-гексадекана (1-ХГД) кислородом воздуха в присутствии двухкомпонентной каталитической системы, состоящей из $St_2Co(OH)$ и *N*-гидроксифталимида (*N*-ГФИ). Расход воздуха при окислении 1-ХГД контролировали газовым счетчиком. Идентификацию, состав и содержание исходного 1-ХГД для контроля конверсии проводили с использованием хромато-масс-спектрометрического анализа на приборе Agilent GC 7820A/MSD 5975. Строение гидроксистеарата кобальта(III) подтверждено инфракрасной спектроскопией.

Результаты. Исследование двухкомпонентной каталитической системы $St_2Co(OH)$–*N*-ГФИ в реакции окисления 1-ХГД кислородом воздуха показало, что оба компонента каталитической системы участвуют в процессе образования гидропероксидов, что значительно ускоряет их образование и способствует созданию высоких содержаний гидропероксидов в реакционной массе. Установлено, что $St_2Co(OH)$ в составе двухкомпонентной каталитической системы ускоряет реакцию разложения гидропероксидов лучше, чем St_2Co в составе изученной нами ранее двухкомпонентной каталитической системы St_2Co–*N*-ГФИ. Полученные оксидаты могут служить сырьем для создания многофункциональных добавок для переработки поливинилхлорида.

Выводы. Установлено, что для жидкофазного окисления 1-ХГД кислородом воздуха двухкомпонентная каталитическая система $St_2Co(OH)$–*N*-ГФИ является более эффективной, чем двухкомпонентная каталитическая система St_2Co–*N*-ГФИ. Найдено, что для жидкофазного окисления 1-ХГД кислородом воздуха оптимальное содержание двухкомпонентной каталитической системы $St_2Co(OH)$–*N*-ГФИ в реакционной массе составляет 9 мол. % от загрузки сырья при мольном соотношении компонентов 1 : 6. Такая каталитическая система позволяет получать кислотное число в оксидате 42 мгКОН/г через 10 ч окисления.

Ключевые слова

1-хлор-*н*-гексадекан, жидкофазное каталитическое окисление, двухкомпонентная каталитическая система, гидроксистеарат кобальта, *N*-гидроксифталимид, гидропероксид, конверсия, кислотное число, карбоновые кислоты

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INTRODUCTION

We have previously shown that liquid-phase catalytic low-temperature oxidation of chlorinated paraffins and long-chain normal monohaloalkanes with atmospheric oxygen produces oxidates containing, among other things, carboxylic acids which can be used as multifunctional additives for processing polyvinyl chloride (PVC) [1–3]. Such multifunctional additives, as a rule, have low toxicity [4], exhibit the properties of plasticizers, stabilizers, lubricants, and impart useful properties to products based on PVC [5, 6]. Long-chain normal individual monohaloalkanes are also of interest when studying the regularities of processes occurring during their catalytic liquid-phase oxidation. In this case the reaction and composition of the reaction mass are significantly simplified when compared to the oxidation of chlorinated paraffins [3], which are mixtures of chloroalkanes with varying degrees of chlorination.

There is insufficient data in the literature on the oxidation of individual long-chain chlorinated hydrocarbons in the liquid phase with atmospheric oxygen in the presence of organic cobalt salts. Thus, the search for highly effective catalytic systems for aerobic oxidation of long-chain chlorinated alkanes is currently important for theory and practice.

Previously, we used a cobalt(II) stearate catalyst (St_2Co, St = $C_{17}H_{35}COO–$) [7] and a catalytic system consisting of St_2Co and *N*-hydroxyphthalimide (*N*-HPI) [8] for the liquid-phase oxidation of 1-chloro-*n*-hexadecane (1-CHD) with atmospheric oxygen to carboxylic acids.

The aim of this study is to develop a highly effective catalytic system for the liquid-phase oxidation of long-chain monochlorinated alkanes with atmospheric oxygen to a mixture of high-boiling chlorine-containing carboxylic acids which can be used as a raw material for obtaining multifunctional additives for PVC. This catalytic system should be capable of performing oxidation with high conversion, high rate and allow products with high acid number values to be obtained. For this purpose, we have developed a new catalytic system containing $St_2Co(OH)$ and *N*-HFI using the example of 1-CHD oxidation [9]. During oxidation with atmospheric oxygen this system allows a reaction mass (oxidate) to be obtained which contains mainly carboxylic acids, esters, and alcohols with a maximum content of high-boiling chlorine-containing carboxylic acids.

MATERIALS AND METHODS

In this work, we used 1-CHD (*Alfa Aesar*, CAS 4860-03-1, USA). *N*-HPI (*Acros Organics*, CAS 524-38-9, USA), cobalt(II) stearate (*Alfa Aesar*, CAS 1002-88-6, USA), and cobalt(III) hydroxystearate prepared according to the method [10] were used as catalysts. The latter method allows cobalt(III) hydroxystearate to be obtained with a yield of 87–88%.

The infrared spectrum of cobalt(III) hydroxystearate is as follows: ν = 3360–3320 cm^{-1}, (s), stretching vibrations of the OH group; 2970 cm^{-1}, (s), stretching vibrations of CH_3–; 2850–2815 and 2940–2915 cm^{-1}, stretching vibrations of CH_2 groups; 1480 cm^{-1}, (s), deformation vibrations of $–CH_2–$; 720 cm^{-1}, (s), rocking vibrations of $–(CH_2)_n–$; 1710 cm^{-1}, (m), stretching vibrations of the carbonyl group ν(C=O); 1580 cm^{-1}, (s), stretching vibrations of COO^- in carboxylic acid salts; 1410 cm^{-1}, (s), deformation vibrations of $–CH_2–CO$; 580 cm^{-1}, (c), stretching vibrations of Co–O bonds. The spectrum of the salt obtained does not contain absorption bands in the region of 1630–1600 cm^{-1}, as characteristic of coordination or crystallization water.

The oxidation of 1-CHD was carried out in a 150-mL glass column reactor with a length to diameter ratio of 10 : 1 at a specific air flow rate of 65 L/(min · kg of substrate) or more [11]. The initial filling of the reactor volume with the reaction mixture was 46% (69.36 mL). The content of the catalytic system varied from 6 to 12 mol % in the feedstock at a molar ratio of components in the catalytic system of 1 : 6. The results of the studies showed that the repeated use of the St_2Co–*N*-HPI catalytic system decreases the acid number from 26.8 to 10 mg of KOH/g while decreasing the conversion from 21.2 to 8%. The repeated use of the $St_2Co(OH)$–*N*-HPI catalytic system decreases the acid number from 41 to 15 mg of KOH/g, while decreasing the conversion from 31 to 14% after 10 h of oxidation. Thus, a fresh catalytic system was used in all experiments.

The air flow from the compressor was controlled by a gas meter. Air distribution in the reaction mass was carried out by a bubbler with a porous glass diaphragm (porosity 160 μm). Before feeding air into the reactor, it was heated to a reaction temperature of 105°C. As shown previously [11], the operation of the column apparatus switches from the bubbling mode to the foam mode under experimental conditions starting with an air flow rate of 65 L/(min · kg of substrate) and more. The foam mode has the highest specific contact surface, allowing the process to be carried out without diffusional resistance in the kinetic region.

The scheme of the laboratory setup is shown in Fig. 1.

The reactor unit allows light oxidation products carried away by air from the reaction volume to be collected. The exhaust air is bubbled through distilled water to absorb acidic reaction products. In order to avoid breakthrough and maintain a low concentration of absorbed products in the absorbers, the absorbent was replaced with a new portion every 30 min. The acid number was determined for the oxidate in the reactor and for the aqueous solution in the absorbers. The error in determining the acid number of higher carboxylic acids according to GOST 22386-77[1] is 1%.

The identification, composition and content of the initial 1-CHD for conversion control were performed by means of chromatography-mass spectrometric analysis on an Agilent GC 7820A/MSD 5975 instrument

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[1] GOST 22386-77. State Standard of the USSR. Synthetic fatty acids and alcohols. Method for determining acid number. Moscow: State Committee of Standards of the Council of Ministers of the USSR, 1978. 10 p.

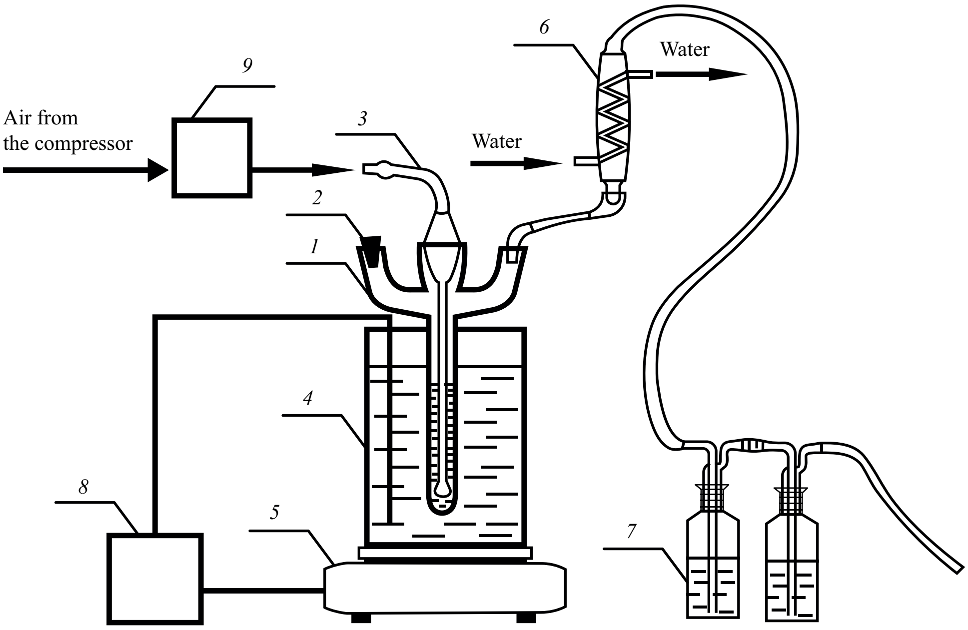


Fig. 1. Setup for liquid-phase oxidation of hexadecane and 1-chlorohexadecane
(*1*) bubbling reactor, column type, length to diameter ratio 10 : 1;
(*2*) fitting for sampling;
(*3*) bubbler;
(*4*) glycerol bath;
(*5*) heating element;
(*6*) refrigerator-condenser,
(*7*) absorber,
(*8*) electronic reactor temperature control unit, and
(*9*) air heating

(*Agilent Technologies*, USA) with a 5-MS quartz capillary column 30 m long, 0.25 mm in diameter. The carrier gas was helium, 1.0 mL/min; injector with a 1 : 5 flow splitter; and injector temperature: 250°C. When programming the capillary column temperature, the initial temperature was 80°C, final temperature, 280°C, isotherm time 10 min; temperature rise rate 10°C/min; and total analysis time 30 min. The detector was a quadrupole mass spectrometer using electron impact ionization with an electron energy of 70 eV in the full mass spectrum scanning mode. The quadrupole temperature was 150°C, and the source temperature was 230°C.

It was found that chlorine was not split off during the oxidation process either from the initial chloroalkane or from the reaction products, i.e., chloracids were present in the oxidate [7]. The acids absorbed in the traps were only derivatives of low-molecular alkanes.

The content of hydroperoxides (wt %) in the reaction mass during oxidation was determined using the method [12]. The accuracy of the analysis was 5% of the relative error of determination [13].

RESULTS AND DISCUSSION

Previously in the process of studying the aerobic oxidation of 1-CHD to carboxylic acids, we developed a two-component catalytic system consisting of cobalt stearate (St_2Co) and *N*-HPI [8]. The optimal molar ratio of the components was found to be 1 : 6. The best results for the acid number in the oxidate (up to 25 mg·KOH/g [8]) were obtained with a content of this catalytic system of 6 mol % in the feedstock, a temperature of 105°C, and an air flow rate of 65 L/(min · kg of substrate) for 5 h of oxidation [8, 11].

Carrying out the oxidation process of 1-CHD under the same conditions, but using a new catalytic system consisting of cobalt hydroxystearate $St_2Co(OH)$ and *N*-HPI, as before, in a molar ratio of 1 : 6, produced better results. Data on the variants of the catalytic system is presented in Table 1, and the results of the experiments, in Fig. 2. For comparison, this figure shows the kinetic curves of 1-CHD oxidation in the presence of the St_2Co–*N*-HPI catalytic system. The data was obtained in [8].

The change in the conversion of 1-CHD over time during its oxidation with atmospheric oxygen at different

Table 1. Variants of the two-component catalytic system $St_2Co(OH)$–*N*-hydroxyphthalimide (*N*-HPI) for the oxidation of 1-chlorohexadecane with air

Characteristics	Experiments			
	1	2	3	4
1-CHD, g	60			
Molar ratio of $St_2Co(OH)$/*N*-HPI in the catalytic system	1 : 6			
Mass content of the catalytic system in the feedstock, wt %	5.3	6.7	7.9	10.6
Molar content of the catalytic system in the feedstock, mol %	6	7.5	9	12
Molar content of the cobalt hydroxystearate catalyst $St_2Co(OH)$, mol % in the catalytic system	0.86	1.07	1.29	1.71
Molar content of the *N*-HPI catalyst, mol % in the catalytic system	5.14	6.43	7.71	10.29

molar contents of catalytic systems in the feedstock is shown in Fig. 2.

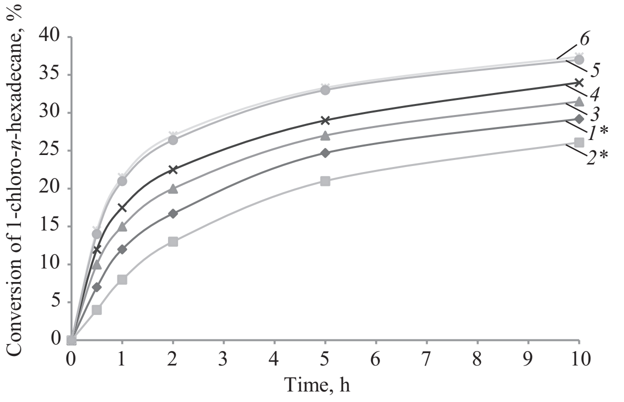


Fig. 2. Dependence of the conversion of 1-chlorohexadecane on time during its oxidation with atmospheric oxygen in the presence of two-component catalytic systems (curves *1** and *2** for the St_2Co–*N*-HPI catalytic system and curves *3*–*6* for the $St_2Co(OH)$–*N*-HPI catalytic system) with their different molar content in raw materials. (*1**) 6; (*2**) 9; (*3*) 6; (*4*) 7.5; (*5*) 9; (*6*) 12 mol % of raw material loading

Comparison of the kinetic curves presented in Fig. 2 shows a significant advantage of the $St_2Co(OH)$–*N*-HPI catalytic system over the St_2Co–*N*-HPI catalytic system. Increasing the content of the $St_2Co(OH)$–*N*-HPI catalytic system from 3 to 9 mol % leads to an increase in the rate of liquid-phase oxidation of 1-CHD and an increase in its conversion over 10 h of the process from 29.2% to 37%. Increasing the content of the new catalytic system over 9 mol % of the feedstock load does not lead to a further increase in the rate of 1-CHD oxidation.

The oxidation of hydrocarbons with atmospheric oxygen to carboxylic acids is known to be a multi-stage process. The result of the first stage of oxidation is the formation of hydroperoxides [14]. The rate of their formation and consumption into intermediate products (alcohols, ketones, aldehydes, etc.) significantly depends on the catalytic systems used.

Figure 3 shows the dependencies of the conversion of 1-CHD and the content of hydroperoxides in the reaction mass on time during liquid-phase oxidation of 1-CHD in the presence of catalytic systems at their optimal content.

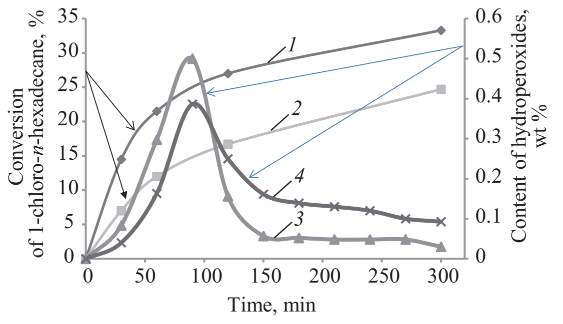


Fig. 3. Dependence of the conversion of 1-chloro-*n*-hexadecane (curves *1* and *2*) and the content of hydroperoxides (curves *3* and *4*) on time during the oxidation of 1-chloro-*n*-hexadecane in the presence of the found optimal content of catalytic systems. Curves *1*, *3* — 9 mol % of the feedstock load of a two-component catalytic system ($St_2Co(OH)$–*N*-HPI in a molar ratio of 1 : 6); *2*, *4* — 6 mol % of the feedstock load of a two-component catalytic system (St_2Co–*N*-HPI in a molar ratio of 1 : 6). Air consumption 65 L/(min·kg of substrate), temperature 105°C

Analysis of Fig. 3 shows that when using the two-component catalytic system $St_2Co(OH)$–*N*-HPI (curve *3*), the rate of hydroperoxide accumulation and consumption is significantly higher than when using the catalytic system St_2Co–*N*-HPI (curve *4*).

It also follows from Fig. 3 that when using the two-component catalytic system $St_2Co(OH)$–*N*-HPI, the average rate of 1-CHD consumption is higher (curve *1*) than in the presence of the catalytic system St_2Co–*N*-HPI (curve *2*). Comparison of curves *1* and *2* with curves *3* and *4* on the same graph shows that as the conversion of 1-CHD increases to 25% (curve *1*), the content of hydroperoxides increases to 0.5% (curve *3*). However, for the St_2Co–*N*-HPI catalytic system with a 1-CHD conversion of 15% (curve *2*), the content of hydroperoxides is only 0.4% (curve *4*).

When using the two-component $St_2Co(OH)$–*N*-HPI catalytic system, the rapid accumulation of hydroperoxides is due to the fact that both *N*-HPI and $St_2Co(OH)$ participate in the chain initiation stage. Both components promote the formation and increase in the concentration of the phthalimide *N*-oxyl radical $PINO^\bullet$. As a result, the formation of hydroperoxides is accelerated and their content in the reaction mass increases.

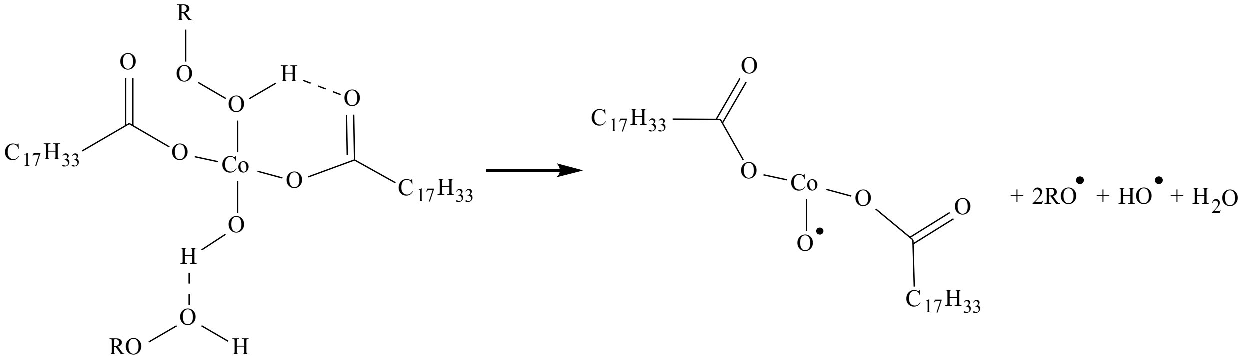
The presence of *N*-HPI in the reaction system also has a significant effect on the selectivity of hydroperoxide formation [15]. Peroxide radicals ($ROO^\bullet$) quickly react with the initial *N*-HPI molecule, thus forming hydroperoxide and *N*-oxyl radical $PINO^\bullet$.

Thus, a decrease in the concentration of peroxide radicals ($ROO^\bullet$) reduces the rate of quadratic chain termination, significantly increasing the selectivity of hydroperoxide formation and, accordingly, reducing the rate of byproduct formation [15].

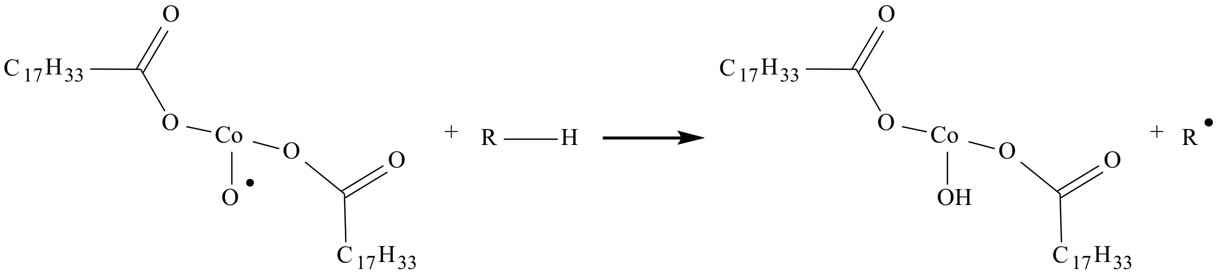
In the presence of the $St_2Co(OH)$–*N*-HPI catalytic system, hydroperoxides were found to decompose more quickly compared to the St_2Co–*N*-HPI catalytic system (Fig. 3). The increase in the rate of hydroperoxides decomposition under the action of the catalytic system $St_2Co(OH)$–*N*-HPI appears to be due to the fact that $St_2Co(OH)$ can participate in the process of hydroperoxides decomposition by forming hydrogen bonds with two hydroperoxide molecules: one hydroperoxide molecule forms a hydrogen bond with carbonyl oxygen, and the second forms a hydrogen bond of the hydroperoxide molecule with the –OH group of $St_2Co(OH)$ (Scheme 1) [16].

The resulting radical $CoSt_2O^\bullet$ quickly transforms into $CoSt_2(OH)$ by interacting with the raw material molecule (Scheme 2).

A mixture of oxygen-containing products (ketones, aldehydes, etc.) is known to be formed in the process of hydroperoxides decomposition. After oxidation, they are converted into carboxylic acids [14]. Figure 4 shows the dependence of the acid number in the oxidate on time.



Scheme 1. Decomposition of hydroperoxides involving $CoSt_2(OH)$



Scheme 2. Regeneration of $CoSt_2(OH)$

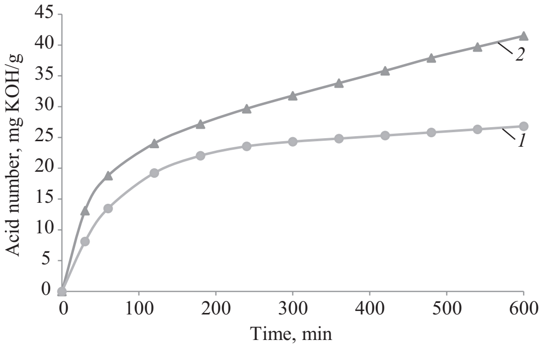


Fig. 4. Dependence of the acid number in the oxidate on time during the oxidation of 1-chlorohexadecane in the presence of catalytic systems: (*1*) 6 mol % of the feedstock load of a two-component catalytic system (St_2Co–*N*-HPI in a molar ratio of 1 : 6); (*2*) 9 mol % of the feedstock load of a two-component catalytic system ($St_2Co(OH)$–*N*-HPI in a molar ratio of 1 : 6). Air consumption 65 L/(min · kg of substrate), temperature 105°C

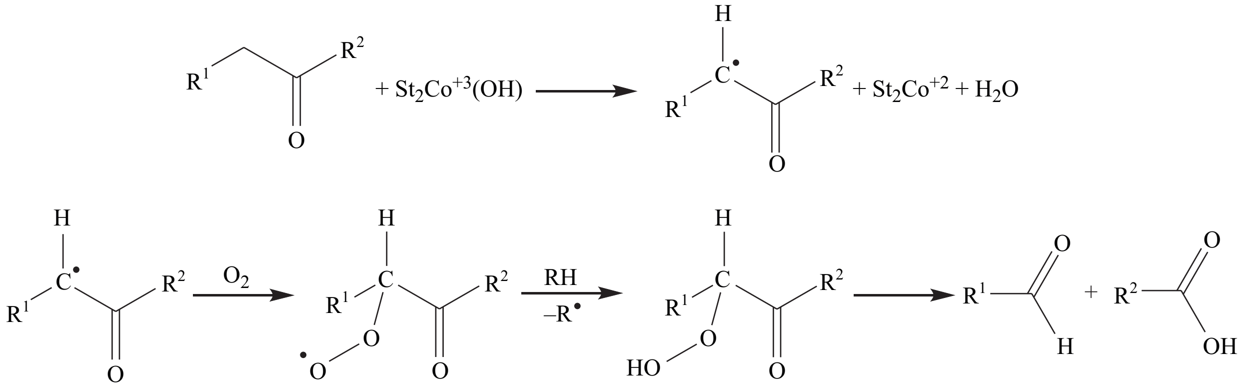
Figure 4 shows that the use of the $St_2Co(OH)$–*N*-HPI catalytic system enables a higher content of carboxylic acids to be obtained at a higher rate than in the presence of the St_2Co–*N*-HPI catalytic system.

Ishii [17] points out that, for example, when oxidizing cyclohexane using the Co(III) catalyst instead of Co(II) at close conversion values, the selectivity of the products (ketones and acids) is always higher. This fact can be explained by the ability of $St_2Co^{+3}(OH)$, as part of the $St_2Co^{+3}(OH)$–*N*-HPI catalytic system, to accelerate the oxidation of intermediate products, for example, ketones into acids according to Scheme 3.

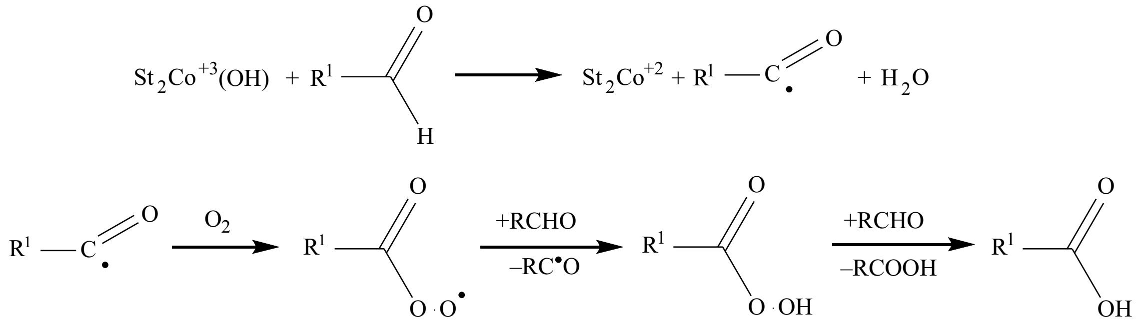
Further, the resulting aldehydes yield acids upon oxidation in the presence of $St_2Co(OH)$ according to Scheme 4.

It has been shown experimentally that the oxidate contains chlorinated and non-chlorinated carboxylic acids (Table 2) in accordance with the presented transformation schemes.

Thus, the presence of $St_2Co(OH)$ in the catalytic system $St_2Co(OH)$–*N*-HPI promotes the acceleration of the formation and consumption of hydroperoxides into intermediate products (ketones, aldehydes, etc.) and their secondary oxidation into carboxylic acids. We also considered 1-CHD, a solvent, as a factor in accelerating the oxidation process. Polar 1-CHD is known to improve the solubility of *N*-HPI [18] while worsening the conditions for micelle formation from cobalt salts, thus enhancing the activity of the catalyst [14].



Scheme 3. Oxidation of intermediate products (ketones) to acids involving $St_2Co(OH)$



Scheme 4. Oxidation of intermediate products (aldehydes) to acids involving $St_2Co(OH)$

Table 2. Composition of acids isolated from the oxidate after 5 h of 1-chloro-*n*-hexadecane oxidation with air in the presence of the catalytic system $St_2Co(OH)$ *N*-HPI

Acids	Molecular weight, *M*, g/mol	Content, %
$CH_3–(CH_2)_{13}–COOH$	242	5.56
$CH_3–(CH_2)_{12}–COOH$	228	1.79
$CH_3–(CH_2)_{11}–COOH$	214	1.49
$CH_3–(CH_2)_{10}–COOH$	200	7.44
$CH_3–(CH_2)_9–COOH$	186	11.71
$CH_3–(CH_2)_8–COOH$	172	14.41
$CH_3–(CH_2)_7–COOH$	158	13.93
$CH_3–(CH_2)_6–COOH$	144	10.38
$Cl–(CH_2)_9–COOH$	206.5	10.89
$Cl–(CH_2)_{10}–COOH$	220.5	8.53
$Cl–(CH_2)_{11}–COOH$	234.5	8.04
$Cl–(CH_2)_{12}–COOH$	248.5	5.84

CONCLUSIONS

The study established that the two-component catalytic system $St_2Co(OH)$–*N*-HPI is more effective for the liquid-phase oxidation of 1-CHD with atmospheric oxygen than the two-component catalytic system St_2Co–*N*-HPI.

The optimal content of the two-component catalytic system $St_2Co(OH)$–*N*-HPI in the reaction system for liquid-phase oxidation of 1-CHD with atmospheric oxygen was found to be 9 mol % of the feedstock load, with a molar ratio of components of 1 : 6. Such a catalytic system enables an acid number in the oxidate of 42 mgKOH/g to be obtained after 10 h of oxidation.

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Authors' contributions

V.N. Sapunov—design of the research concept, discussion and analysis of the results.

Yu.L. Zotov—design of the research concept, development of the experiment, discussion and analysis of the results, writing the text of the article.

Nguyen Thanh Tung—design of the research concept, planning and conducting experimental studies, processing the data obtained, preparation of the data obtained for publication.

Yu.V. Popov—consultation on conducting individual stages of the study, scientific editing.

E.V. Shishkin—consultation on conducting individual stages of the study, scientific editing.

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About the authors

Valentin N. Sapunov, Dr. Sci. (Chem), Professor, Department of Chemical Technology of Basic Organic and Petrochemical Synthesis, Mendeleev University of Chemical Technology of Russia (9, Miusskaya pl., Moscow, 125047, Russia). sapunovvals@gmail.com. Scopus Author ID 7006540459, RSCI SPIN-code 9357-5030, https://orcid.org/0000-0002-1006-5436

Yuriy L. Zotov, Dr. Sci. (Chem.), Professor, Department of Organic and Petrochemical Synthesis Technology, Volgograd State Technical University (28, pr. im. V.I. Lenina, Volgograd, 400005, Russia). E-mail: ylzotov@mail.ru. Scopus Author ID 7003371961, RSCI SPIN-code 7543-9740, http://orcid.org/0000-0001-6301-0570

Nguyen Thanh Tung, Engineer, Department of Organic and Petrochemical Synthesis Technology, Volgograd State Technical University (28, pr. im. V.I. Lenina, Volgograd, 400005, Russia). E-mail: thanhtung92dh@gmail.com. https://orcid.org/0009-0006-7386-8910

Evgeniy V. Shishkin, Dr. Sci. (Chem.), Professor, Department of Organic and Petrochemical Synthesis Technology, Volgograd State Technical University (28, pr. im. V.I. Lenina, Volgograd, 400005, Russia). E-mail: shishkin@vstu.ru. Scopus Author ID 7004314557, RSCI SPIN-code 3280-1800, https://orcid.org/0000-0002-2994-422X

Yuriy V. Popov, Dr. Sci. (Chem.), Professor, Department of Organic and Petrochemical Synthesis Technology, Volgograd State Technical University (28, pr. im. V.I. Lenina, Volgograd, 400005, Russia). E-mail: iury.popov@yandex.ru. Scopus Author ID 26028090100, RSCI SPIN-code 4582-3342, http://orcid.org/0000-0001-5659-028X

Об авторах

Сапунов Валентин Николаевич, д.х.н., профессор кафедры химической технологии основного органического и нефтехимического синтеза, ФГБОУ ВО «Российский химико-технологический университет им. Д.И. Менделеева» (125047, Россия, Москва, Миусская пл., д. 9). E-mail: sapunovvals@gmail.com. Scopus Author ID 7006540459, SPIN-код РИНЦ 9357-5030, https://orcid.org/0000-0002-1006-5436

Зотов Юрий Львович, д.х.н., профессор кафедры технологии органического и нефтехимического синтеза, ФГБОУ ВО «Волгоградский государственный технический университет» (400005, Россия, Волгоград, пр-т им. В.И. Ленина, д. 28). E-mail: ylzotov@mail.ru. Scopus Author ID 7003371961, SPIN-код РИНЦ 7543-9740, http://orcid.org/0000-0001-6301-0570

Нгуен Тхань Тунг, инженер, кафедра технологии органического и нефтехимического синтеза, ФГБОУ ВО «Волгоградский государственный технический университет» (400005, Россия, Волгоград, пр-т им. В.И. Ленина, д. 28). E-mail: thanhtung92dh@gmail.com. https://orcid.org/0009-0006-7386-8910

Шишкин Евгений Вениаминович, д.х.н., профессор кафедры технологии органического и нефтехимического синтеза, ФГБОУ ВО «Волгоградский государственный технический университет» (400005, Россия, Волгоград, пр-т им. В.И. Ленина, д. 28). E-mail: shishkin@vstu.ru. Scopus Author ID 7004314557, SPIN-код РИНЦ 3280-1800, https://orcid.org/0000-0002-2994-422X

Попов Юрий Васильевич, д.х.н., профессор кафедры технологии органического и нефтехимического синтеза, ФГБОУ ВО «Волгоградский государственный технический университет» (400005, Россия, Волгоград, пр-т им. В.И. Ленина, д. 28). E-mail: iury.popov@yandex.ru. Scopus Author ID 26028090100, SPIN-код РИНЦ 4582-3342, http://orcid.org/0000-0001-5659-028X

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