Tonkie Khimicheskie Tekhnologii = Fine Chemical Technologies.
2024;19(3):192–201

ISSN 2686-7575 (Online)

Chemistry and technology of organic substances

Химия и технология органических веществ

UDC 66.095.62+547.295.3+544.47+544.478.1
https://doi.org/10.32362/2410-6593-2024-19-3-192-201
EDN SYTFBD

CC BY

RESEARCH ARTICLE

Effect of 2-hexanol and methanol on the *one-pot* process of dehydration and alkoxycarbonylation for the synthesis of esters

Nadezhda T. Sevostyanova✉, Sergey A. Batashev, Anastasia S. Rodionova, Dar'ya K. Kozlenko

Tula State Lev Tolstoy Pedagogical University, Tula, 300026 Russia

✉ *Corresponding author, e-mail: sevostyanova.nt@gmail.com*

Abstract

Objectives. To study the possibility of *one-pot* synthesis (combination of two processes in one reactor) for the following pairs of processes: (1) dehydration of 2-hexanol and isomerizing alkoxycarbonylation of the resulting 2-hexene, in order to obtain 2-hexyl heptanoate, and (2) dehydration of 2-hexanol and isomerizing methoxycarbonylation of the resulting 2-hexene, in order to obtain methyl esters of C_7 carboxylic acids. To investigate the effect of the concentrations of 2-hexanol and methanol on the rate of the *one-pot* synthesis.

Methods. *One-pot* synthesis was studied in a toluene medium in a steel batch reactor designed to operate at elevated pressure and equipped with a glass insert, a magnetic stirrer, a sampler, and gas input and discharge devices. Samples of the reaction mass were taken during the combined process and were analyzed by means of gas–liquid chromatography with a flame ionization detector.

Results. The possibility of *one-pot* combination was demonstrated for 2-hexanol dehydration catalyzed by methanesulfonic acid, as well as for the isomerizing alkoxycarbonylation of the resulting 2-hexene with 2-hexanol and CO, catalyzed by the $Pd(PPh_3)_2Cl_2$–XANTPHOS–methanesulfonic acid system. The dependencies of the rates of the dehydration of 2-hexanol and the formation of esters of C_7 carboxylic acids on the concentration of 2-hexanol were shown to pass through a maximum. The possibility of the *one-pot* process was proved for the synthesis of esters from 2-hexanol, methanol, and CO with the predominant formation of heptanoic acid esters in the presence of the above catalytic system. The rates of dehydration of 2-hexanol and the formation of 2-hexyl esters of C_7 carboxylic acids were found to decrease with increasing the concentration of methanol in the reaction mass. Under mild conditions (temperature 115°C, CO pressure 3 MPa) with the addition of methanol, the total fraction of 2-hexyl and methyl heptanoic acid esters among C_7 carboxylic acid esters was determined to be 85.5%.

Conclusions. The reactions of intramolecular acid–catalytic dehydration of 2-hexanol and isomerizing alkoxycarbonylation of the resulting 2-hexene, catalyzed by the $Pd(PPh_3)_2Cl_2$–XANTPHOS–methanesulfonic acid system, can be performed as a *one-pot* process. Methanesulfonic acid simultaneously functions as a catalyst for the dehydration of 2-hexanol and a cocatalyst for the palladium–phosphine system for the alkoxycarbonylation of hexenes. In the presence of the $Pd(PPh_3)_2Cl_2$–XANTPHOS–methanesulfonic acid catalytic system, processes for the synthesis of heptanoic acid esters from 2-hexanol, methanol, and CO can be combined within one reactor. An increase in the methanol concentration negatively affects the rate of the dehydration of 2-hexanol and the formation of 2-hexyl esters of C_7 carboxylic acids. A small amount of methanol in the reaction mass leads to an increase in the fraction of heptanoic acid esters among C_7 carboxylic acid esters.

Keywords

one-pot synthesis, ester synthesis, alcohol dehydration, isomerizing alkoxycarbonylation, 2-hexanol, methanol, palladium catalyst, XANTPHOS diphosphine, methanesulfonic acid

Submitted: 07.09.2023
Revised: 30.01.2024
Accepted: 17.04.2024

For citation

Sevostyanova N.T., Batashev S.A., Rodionova A.S., Kozlenko D.K. Effect of 2-hexanol and methanol on the *one-pot* process of dehydration and alkoxycarbonylation for the synthesis of esters. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2024;19(3):192–201. https://doi.org/10.32362/2410-6593-2024-19-3-192-201

© N.T. Sevostyanova, S.A. Batashev, A.S. Rodionova, D.K. Kozlenko, 2024

НАУЧНАЯ СТАТЬЯ

Влияние гексанола-2 и метанола на совмещенный процесс дегидратации и алкоксикарбонилирования для синтеза сложных эфиров

Н.Т. Севостьянова✉, С.А. Баташев, А.С. Родионова, Д.К. Козленко
Тульский государственный педагогический университет им. Л.Н. Толстого, Тула, 300026 Россия
✉ *Автор для переписки, e-mail: sevostyanova.nt@gmail.com*

Аннотация

Цели. Изучить возможности совмещения в одном реакторе процессов: 1) дегидратации гексанола-2 и изомеризующего алкоксикарбонилирования образующегося гексена-2 для получения 2-гексилгептаноата; 2) дегидратации гексанола-2 и изомеризующего метоксикарбонилирования образующегося гексена-2 для получения метиловых эфиров карбоновых кислот C_7. Исследовать закономерности влияния концентрации гексанола-2 и метанола на скорость совмещенного процесса.

Методы. Совмещенный процесс изучали в среде толуола в периодическом стальном реакторе, рассчитанном на работу при повышенном давлении, снабженном стеклянной вставкой, магнитной мешалкой, пробоотборником, устройствами ввода и сброса газов. Отбираемые в ходе совмещенного процесса пробы реакционной массы анализировали методом газо-жидкостной хроматографии с пламенно-ионизационным детектором.

Результаты. Показана возможность совмещения в одном реакторе дегидратации гексанола-2, катализируемой метансульфокислотой, и изомеризующего алкоксикарбонилирования образующегося гексена-2 гексанолом-2 и CO, катализируемого системой $Pd(PPh_3)_2Cl_2$–XANTPHOS–метансульфокислота. Установлены экстремальные зависимости скоростей дегидратации гексанола-2 и образования сложных эфиров карбоновых кислот C_7 от концентрации гексанола-2. Показана возможность реализации совмещенного в одном реакторе процесса синтеза сложных эфиров из гексанола-2, метанола и CO с преимущественным образованием сложных эфиров гептановой кислоты в присутствии указанной каталитической системы. Обнаружено снижение скоростей дегидратации гексанола-2 и образования 2-гексиловых эфиров карбоновых кислот C_7 с увеличением концентрации метанола в реакционной массе. В мягких условиях (температура 115°C, давление CO 3 МПа) в присутствии добавок метанола определена суммарная доля 2-гексилового и метилового эфиров гептановой кислоты среди сложных эфиров карбоновых кислот C_7, которая составила 85.5%.

Выводы. Реакции внутримолекулярной кислотно-каталитической дегидратации гексанола-2 и изомеризующего алкоксикарбонилирования образующегося гексена-2, катализируемого системой $Pd(PPh_3)_2Cl_2$–XANTPHOS–метансульфокислота, могут быть совмещены в одном реакторе. Метансульфокислота одновременно выполняет функции катализатора дегидратации гексанола-2 и сокатализатора палладий-фосфиновой системы алкоксикарбонилирования гексенов. В присутствии каталитической системы $Pd(PPh_3)_2Cl_2$–XANTPHOS–метансульфокислота могут быть реализованы в одном реакторе процессы синтеза сложных эфиров гептановой кислоты из гексанола-2, метанола и CO. Увеличение концентрации метанола негативно влияет на скорости дегидратации гексанола-2 и образование 2-гексиловых эфиров карбоновых кислот C_7. Небольшие количества метанола в реакционной массе приводят к увеличению доли сложных эфиров гептановой кислоты среди сложных эфиров карбоновых кислот C_7.

Ключевые слова
совмещенный процесс, синтез сложного эфира, дегидратация спирта, изомеризующее алкоксикарбонилирование, гексанол-2, метанол, палладиевый катализатор, дифосфин XANTPHOS, метансульфокислота

Поступила: 07.09.2023
Доработана: 30.01.2024
Принята в печать: 17.04.2024

Для цитирования
Севостьянова Н.Т., Баташев С.А., Родионова А.С., Козленко Д.К. Влияние гексанола-2 и метанола на совмещенный процесс дегидратации и алкоксикарбонилирования для синтеза сложных эфиров. *Тонкие химические технологии.* 2024;19(3):192–201. https://doi.org/10.32362/2410-6593-2024-19-3-192-201

INTRODUCTION

CO-based syntheses are used to obtain a wide range of organic products. For example, carbonylation of alcohols and alkoxycarbonylation of unsaturated compounds give esters. In the former case, it is mainly homogeneous catalysts based on rhodium and iridium compounds with the addition of iodides which are used, since not alcohols, but alkyl iodides are directly carbonylated [1, 2]. These processes primarily use methanol and ethanol which produce carboxylic acids and esters as the main products, and hydrocarbons and ethers as by-products. In the latter case, the most active catalysts are considered to be homogeneous systems based on palladium compounds with organophosphine and H-acid promoters. In the presence of such systems, alkoxycarbonylation yields only isomeric esters [3, 4]. The alkoxycarbonylation of alkenes, which occurs with the cleavage of the C–C π bond, is energetically preferable to carbonylation of alcohol, which requires the cleavage of the C–O σ bond. However, some alcohols are more accessible than alkenes. Previously "*one-pot* synthesis" (combination of two processes in one reactor) was shown to be possible for the dehydration of (primary and secondary) alcohols and carbonylation of the resulting alkenes to form esters and carboxylic acids in the presence of homogeneous palladium catalysts and *p*-toluenesulfonic acid (TsOH) [5–8]. In particular, a *one-pot* process based on cyclohexanol and CO was carried out in the presence of homogeneous catalytic systems based on $Pd(PPh_3)_2Cl_2$ [6], $PdCl_2$ [7], and $Pd(OAc)_2$ [8] in combination with the promoting additive PPh_3 and TsOH. TsOH was a catalyst for the dehydration of cyclohexanol and a cocatalyst for the alkoxycarbonylation of cyclohexene. However, of practical interest is the synthesis of esters of aliphatic acids, primarily, of a linear structure, which as a rule are of the greatest value. For example, heptanoates and decanoates are components of hormonal drugs (testosterone preparations) [9]. High selectivities for esters of linear carboxylic acids are achieved in alkoxycarbonylation catalyzed by means of palladium systems with some diphosphines, mainly *tert*-butyl-substituted diphosphines [10–16] and diphosphines of the XANTPHOS group[1] [17, 18]. These include in the case of alkenes with internal position of the C=C bond (isomerizing alkoxycarbonylation). Isomerizing alkoxycarbonylation consists of two stages: migration of a multiple bond from the internal position to the terminal position and subsequent alkoxycarbonylation to form an ester with a mainly linear structure.

The purpose of this work was to study the possibility of *one-pot* combination of the following processes (Fig. 1): (1) dehydration of 2-hexanol (**1**) and isomerizing alkoxycarbonylation of the resulting 2-hexene (**2**), in order to obtain 2-hexyl heptanoate (product **3a**, reactions (1), (2)); and (2) dehydration of alcohol **1** and isomerizing methoxycarbonylation of alkene **2**, in order to form methyl esters of C_7 carboxylic acids (products **4a**–**4c**, reactions (1), (3)) aimed at increasing the rate of the process of obtaining esters; as well as to investigate the effect of the concentration of alcohol **1** and methanol on the rate of the *one-pot* process of ester synthesis.

The catalyst used in the *one-pot* processes being study was the $Pd(PPh_3)_2Cl_2$–XANTPHOS–methanesulfonic acid (MsOH) system. This catalytic precursor was chosen due to its highest level of activity in a model *one-pot*

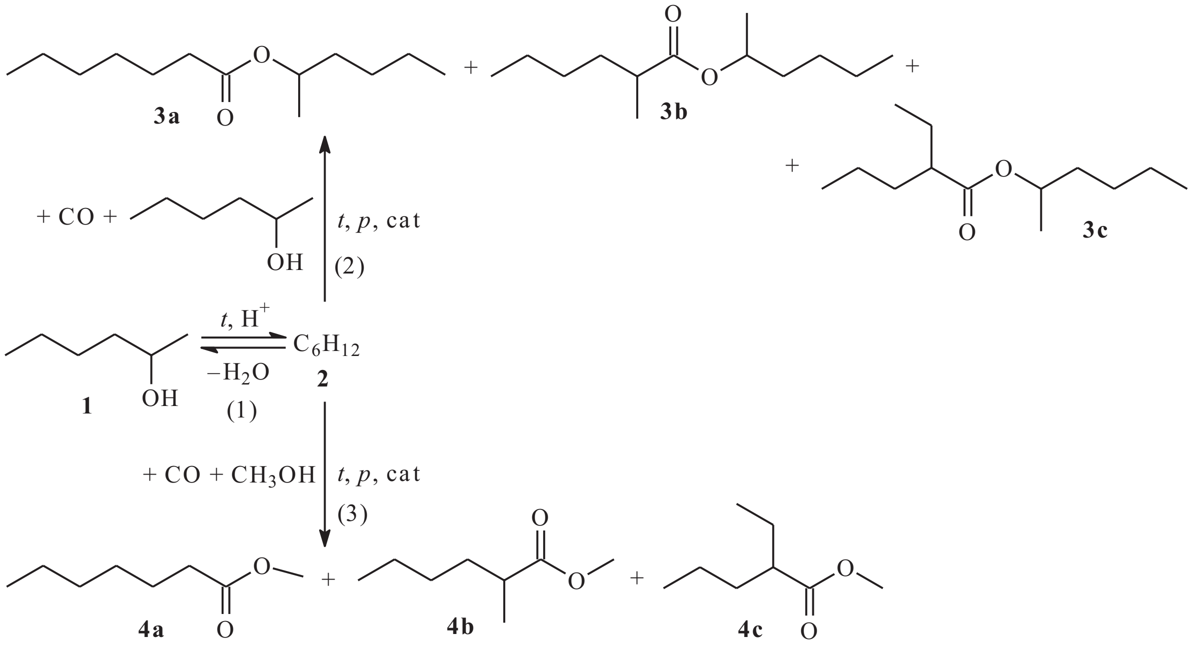


Fig. 1. Scheme of the *one-pot* synthesis of esters from 2-hexanol, methanol, and CO

---

[1] XANTPHOS is an organophosphorus compound $C_{39}H_{32}OP_2$ obtained from heterocyclic xanthene.

process based on cyclohexanol and CO in comparison with $PdCl_2$ and $Pd(OAc)_2$ [6–8]. XANTPHOS and MsOH were used as components of catalytic systems for isomerizing alkoxycarbonylation [17, 18].

EXPERIMENTAL

The *one-pot* process was studied in a toluene medium (*Komponent-Reaktiv*, Russia) in a steel batch reactor (Russia) according to the published procedure [8]. During the experiments, the temperature was maintained at 115°C, and the pressure of a 1 : 1 mixture of CO (*BK Group*, Russia) and Ar (*Arton*, Russia) was 6.1 MPa. The concentrations of the components of the catalytic system were as follows, mol/L: $C(Pd(PPh_3)_2Cl_2) = 2.0 \cdot 10^{-3}$ (*TCI*, Japan), C(XANTPHOS) = $= 2.5 \cdot 10^{-3}$ (*BIOSYNTH CARBOSYNTH*, USA), and C(MsOH) = 0.16 (*Sigma-Aldrich*, France).

Samples of the reaction mass were taken during each experiment and were analyzed by means of gas–liquid chromatography with a Crystallux-4000M chromatograph (*Meta-Chrom*, Russia) with a flame ionization detector and argon carrier gas. The carrier gas flow rate was 1.0 mL/min; and the flow splitting 1 : 60. The evaporator and detector temperatures were 300 and 320°C, respectively. The components of the reaction mass were separated in an Optima-5 capillary column (*MACHEREY–NAGEL*, Germany); 30 m × 0.32 mm; film thickness 0.35 µm; temperature programming mode: isothermal mode 80°C for 5 min, in the range 80–220°C at a heating rate of 20 deg/min, in the range 220–280°C at a heating rate of 8 deg/min, isothermal mode 280°C for 2.5 min. Peak areas were calculated using the NetChrom[2] program. The chromatogram peaks were identified by retention time by comparing them with the retention times of standard samples of substances. The concentrations of substances **1**–**4** were calculated by the internal standard method and decane was used as an internal standard (*EKOS-1*, Russia). The internal standard was introduced at a constant concentration into the reaction solution in toluene before the start of the experiment. Toluene was chosen as a medium for the *one-pot* synthesis as the most commonly used solvent for alkoxycarbonylation processes [6–8, 15, 19–22]. Insignificant (total yield of no more than 8%) amounts of ethers, heptanoic acid, and 2-methylhexanoic acid were formed as by-products.

RESULTS AND DISCUSSION

The possibility of the *one-pot* combination of the dehydration of alcohol **1** and the alkoxycarbonylation of resulting alkene **2** was tested in experiments 1 and 2 (Table 1). The most reactive of all alcohols in alkoxycarbonylation is known to be methanol [23]. In this regard, the *one-pot* synthesis was performed using both alcohol **1** and methanol (Table 1, experiments 3, 4). The yields of products **3a**–**3c** were calculated by the formula:

$$\eta(\mathbf{3a}–\mathbf{3c}) = \frac{C(\mathbf{3a}–\mathbf{3c})}{0.5C(\mathbf{1})} \cdot 100\%, \quad (A)$$

wherein $C(\mathbf{1})$ is the initial concentration of alcohol **1**, mol/L; $C(\mathbf{3a}–\mathbf{3c})$ are the concentrations of esters at the end of the process, mol/L.

The yields of products **4a**–**4c** were calculated by the formula:

$$\eta(\mathbf{4a}–\mathbf{4c}) = \frac{C(\mathbf{4a}–\mathbf{4c})}{C(CH_3OH)} \cdot 100\%, \quad (B)$$

wherein $C(CH_3OH)$ is the initial concentration of methanol, mol/L; $C(\mathbf{4a}–\mathbf{4c})$ is the concentrations of esters at the end of the process, mol/L.

Table 1. Results of the study of *one-pot* processes based on alcohol **1** and CO (experiments 1 and 2), as well as alcohol **1**, methanol, and CO (experiments 3 and 4); the time of the processes was 7 h

Exp. No.	C(**1**), M	$C(CH_3OH)$, M	Product yield, %				Conversion of alcohol **1**, %
			3a	**3(a+b+c)**	**4a**	**4(a+b+c)**	**1**
1	0.500	–	36.1	60.3	–	–	94.7
2	1.000	–	10.4	20.0	–	–	39.5
3	0.250	0.250	10.7	13.7	13.9	15.6	66.4
4	0.500	0.500	5.4	7.2	5.1	6.1	42.3

---

[2] https://www.meta-chrom.ru/catalog/soft/netchrom/. Accessed February 28, 2024.

Table 2. Initial rates of alcohol **1** dehydration (r_1), formation of product **3a** (r_{3a}), and formation of the sum of products **3a**+**3b**+**3c** ($r_{3a+3b+3c}$) in experiments 1, 2, and 5–7

Exp. No.	C(**1**), mol/L	$r_1 \cdot 10^2$, mol/(L·min)	$r_{3a} \cdot 10^4$, mol/(L·min)	$r_{3a+3b+3c} \cdot 10^4$, mol/(L·min)
1	0.500	1.70	2.2	3.0
2	1.000	0.85	0.9	1.3
5	0.150	0.26	0.6	0.7
6	0.300	1.21	2.5	3.5
7	0.750	1.01	1.6	2.2

The conversions of alcohol **1** and methanol were calculated by the formula:

$$\eta(\mathbf{1},\mathrm{CH_3OH}) = \frac{C'(\mathbf{1},\mathrm{CH_3OH})}{C(\mathbf{1},\mathrm{CH_3OH})} \cdot 100\%, \qquad \text{(C)}$$

wherein C’(**1**, CH_3OH) is the concentration of alcohols at the end of the process, mol/L.

As the data in Table 1 shows, in the presence of methanol, the yields of products **3**(**a**+**b**+**c**) decreased, and the total yield of methyl and 2-hexyl esters was also lower when compared with experiments 1 and 2. The intermediate products in all experiments were 1-hexene and 2-hexene. The by-products were heptanoic acid, 2-methylhexanoic acid, and also ethers.

The effect of the concentration of alcohol **1** on the rate of the *one-pot* synthesis of ester products **3a**–**3c** was studied in a series of one-factor experiments (Table 2, experiments 1, 2, 5–7). This consisted of varying the concentration of alcohol **1** in a toluene medium and keeping other reaction conditions constant (in the absence of methanol). Table 2 presents the initial rates of the dehydration of alcohol **1** (r_1), the formation of product **3a** (r_{3a}), and the formation of the sum of products **3a**+**3b**+**3c** ($r_{3a+3b+3c}$) in the *one-pot* process. The rate r_1 was calculated from the slope of the initial portion of the curve for the total formation of free hexenes, esters, heptanoic acid, and 2-methylhexanoic acid. The rates of ester formation were calculated from the slopes of the initial portions of their accumulation curves.

As the data in Table 2 shows, the dehydration rate reached its highest value at an alcohol **1** concentration of 0.500 mol/L. The rates of ester formation were the highest at C(**1**) = 0.300 mol/L. The fraction of product **3a** among resulting esters **3a**–**3c** ranged from 57.5% at C(**1**) = 0.300 M to 74.7% at C(**1**) = 0.15 M. The conversion of alcohol **1** in the latter case reached 89.7%.

At the next stage of research, the effect of methanol on the *one-pot* process was studied in a series of one-factor experiments. This process simultaneously involved alcohol **1**, methanol, and CO. In these experiments (Table 3, experiments 4, 8–11), the concentration of methanol was varied, and the initial concentration of alcohol **1** was 0.500 M. Table 3 presents data on changes in the initial rate of the dehydration of alcohol **1**. Figure 2 illustrates the dependencies of the initial rates of the formation of products **3a**–**3c** and **4a**–**4c**.

Table 3. Initial rates of alcohol **1** dehydration in experiments 4 and 8–11 with the addition of methanol; in all experiments, C(**1**) = 0.500 M

Exp. No.	$C(\mathrm{CH_3OH})$, mol/L	$r_1 \cdot 10^2$, mol/(L·min)
8	0.025	1.48
9	0.050	1.29
10	0.150	1.10
11	0.300	0.90
4	0.500	0.78

Note: experiments are listed in order of increasing methanol concentration.

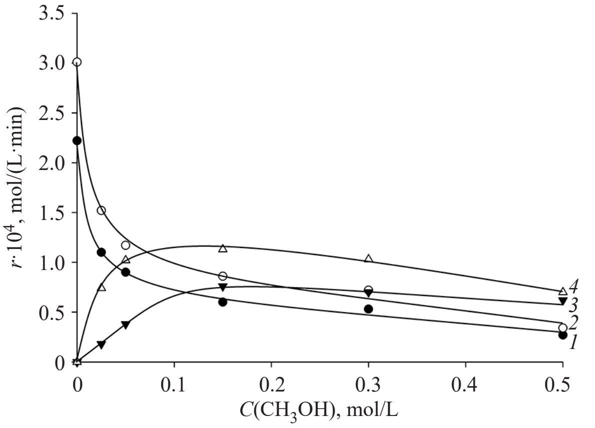
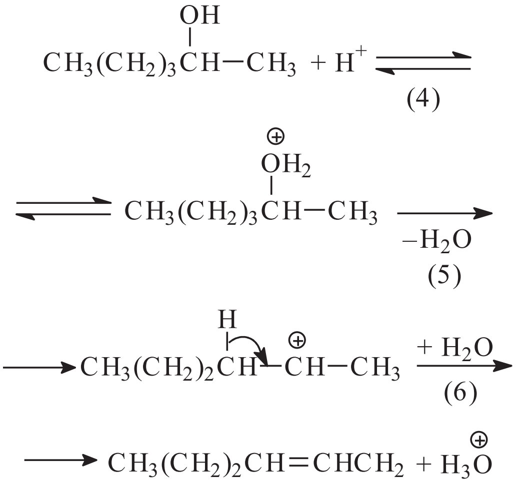


Fig. 2. Dependencies of the rates of the formation of products (*1*) **3a**, (*2*) **3a**+**3b**+**3c**, (*3*) **4a**, and (4) **4a**+**4b**+**4c** in the *one-pot* process based on alcohol **1**, methanol, and CO

As the data in Table 3 (in comparison with the results of experiment 1, Table 2) and Fig. 2 shows, an increase in methanol concentration led to a decrease in the rates of the dehydration of alcohol **1**, the formation of product **3a**, and the formation of the sum of products **3a**+**3b**+**3c**. The dependencies of the rates of the formation of products **4a**, **4b**, and **4c** passed through a maximum. The total fraction of products **3a** and **4a** among the resulting esters ranged from 53.7% at $C(CH_3OH) = 0.025$ M to 80.3% at $C(CH_3OH) = 0.50$ M. However, the conversion of alcohol **1** in the latter case was only 42.3%. In experiments 1–10, the fraction of products **3a**+**4a** among the various esters was the largest (85.5%) in experiment 3.

Liquid-phase dehydration of secondary alcohols under conditions of acid catalysis occurs by the *E*1 mechanism [24]:



$$CH_3(CH_2)_3\overset{OH}{\overset{|}{C}}H-CH_3 + H^+ \rightleftharpoons \tag{4}$$

$$\rightleftharpoons CH_3(CH_2)_3\overset{\overset{\oplus}{OH_2}}{\overset{|}{C}}H-CH_3 \xrightarrow[-H_2O]{} \tag{5}$$

$$\longrightarrow CH_3(CH_2)_2\overset{H}{\overset{|}{C}}H-\overset{\oplus}{C}H-CH_3 \xrightarrow{+H_2O} \tag{6}$$

$$\longrightarrow CH_3(CH_2)_2CH=CHCH_2 + H_3\overset{\oplus}{O}$$

The dehydration of alcohols is known to be complicated by side reactions of the formation of ethers. In our studies, an increase in the concentration of alcohol **1** to 0.500 M led to an increase in the rate of dehydration. With a further increase in the concentration of alcohol **1**, solvation of the carbocation formed in reaction (5) by molecules of alcohol **1** apparently progressed, resulting in the formation of by-products (ethers) and a decrease in the rate of intramolecular dehydration. Under the action of methanol, these negative processes probably occur more actively, resulting in a decrease in the rate of the formation of hexenes as the methanol concentration is increased.

By-products of heptanoic and 2-methylhexanoic acids can be formed in two ways: by the hydrolysis of esters **3a**, **3b**, **4a**, and **4b** and the hydroxycarbonylation of 1-hexene and 2-hexene. This is similar to that described previously for the *one-pot* process based on cyclohexanol and CO [7, 8].

The established dependencies of the rates of the formation of products **3a**–**3c** in the *one-pot* process based on 2-hexanol and CO, as well as those of products **4a**–**4c** in the *one-pot* process based on 2-hexanol, methanol, and CO, pass through a maximum. This is consistent with the data on the alkoxycarbonylation of cyclohexene using cyclohexanol and methanol, catalyzed by the $Pd(PPh_3)_2Cl_2$–PPh_3–TsOH system [21, 22]. The ascending branches of such dependencies are due to the participation of alcohols as co-reagents in alkoxycarbonylation. The descending branches appear to be associated with the involvement of these components in ligand-exchange reactions leading to the formation of catalytically inactive palladium complexes (reactions (7), (8)) [21, 22].

$$Pd(PPh_3)_2(Tol)_2 + ROH \rightleftharpoons Pd(PPh_3)_2(ROH)(Tol) + Tol \tag{7}$$

$$Pd(PPh_3)_2(Tol)_2 + 2ROH \rightleftharpoons Pd(PPh_3)_2(ROH)_2 + 2Tol \tag{8}$$

The decrease in the rates of the formation of products **3a** and **3a**+**3b**+**3c** and the total rate of the formation of esters **3a**+**3b**+**3c**+**4a**+**4b**+**4c** in the presence of methanol is presumably a consequence of a decrease in the rate of the dehydration of alcohol **1.** At the same time the addition of methanol leads to an increase in the fraction of linear esters.

CONCLUSIONS

The possibility of *one-pot* combination was determined for the intramolecular acid-catalytic dehydration of alcohol **1** and the isomerizing alkoxycarbonylation of the resulting 2-hexene, catalyzed by the $Pd(PPh_3)_2Cl_2$–XANTPHOS–MsOH system. MsOH simultaneously served as a catalyst for the dehydration of 2-hexanol and a cocatalyst for the palladium–phosphine system of alkoxycarbonylation of hexenes. The dependencies of the rates of the dehydration of alcohol **1** and the formation of 2-hexyl esters of C_7 carboxylic acids on concentration of alcohol **1** were shown to pass through a maximum. The main product of the *one-pot* process was 2-hexyl heptanoate. The rates of the dehydration of alcohol **1** and the formation of 2-hexyl esters of C_7 carboxylic acids were found to decrease with increasing methanol concentration. The dependencies of the rates of the formation of methyl esters of C_7 carboxylic acids on the concentration of methanol were demonstrated to pass through a maximum. The highest selectivities for heptanoic acid esters (up to 85.5%) were obtained at a molar ratio of 2-hexanol : CH_3OH = 1 : 1. Thus, further studies of the *one-pot* process based on 2-hexanol and CO with the addition of methanol should be aimed at finding optimal conditions, in order to ensure high yields of heptanoic acid esters.

Acknowledgments

The study was supported by the Russian Science Foundation (grant No. 22-23-00102), https://rscf.ru/project/22-23-00102/.

Authors' contributions

N.T. Sevostyanova—the idea of organizing the *one-pot* process, analysis and interpretation of the received data, and writing the text of the article.

S.A. Batashev—chromatographic analysis of the reaction mass, analysis and interpretation of the received data, and participation in writing the article.

A.S. Rodionova—experimental studies of the *one-pot* process with sampling of the reaction mass, calculations based on the experimental results, and participation in writing the article.

D.K. Kozlenko—experimental studies of the *one-pot* process with sampling of the reaction mass, calculations based on the experimental results, and participation in writing the article.

The authors N.T. Sevostyanova, S.A. Batashev, A.S. Rodionova, and D.K. Kozlenko confirm that there is no real or potential conflict of interest in relation to this article.

REFERENCES

1. Kalck P., Le C., Serp B.P. Recent advances in the methanol carbonylation reaction into acetic acid. *Coord. Chem. Rev.* 2020;402:213078. https://doi.org/10.1016/j.ccr.2019.213078
2. Sevostyanova N.T., Batashev S.A. Catalysts for Carbonylation of Alcohols to Obtain Carboxylic Acids and Esters. *Russ. J. Appl. Chem.* 2022;95(8):1085–1106. https://doi.org/10.1134/S107042722208002X
   [Original Russian Text: Sevostyanova N.T., Batashev S.A. Catalysts for Carbonylation of Alcohols to Obtain Carboxylic Acids and Esters. *Zhurnal Prikladnoi Khimii.* 2022;95(8):947–970 (in Russ.). https://doi.org/10.31857/S0044461822080011]
3. Sevostyanova N.T., Batashev S.A. Alkoxycarbonylation of unsaturated phytogenic substrates using palladium catalysts as a way for obtaining ester products. *Kataliz v Promyshlennosti.* 2023;23(1):37–55 (in Russ). https://doi.org/10.18412/1816-0387-2023-1-37-55
4. Liang W.-Y., Liu L., Zhou Q., Yang D., Lu Y., Liu Y. Pd-catalyzed alkoxycarbonylation of alkenes promoted by H_2O free of auxiliary acid additive. *Mol. Catal.* 2020;482:110221. https://doi.org/10.1016/j.mcat.2018.10.016
5. Eliseev O.L., Bondarenko T.N., Stepin N.N., Lapidus A.L. Carbonylation of alcohols in the $Pd(OAc)_2$/TsOH/molten salt system. *Mendeleev Commun.* 2006;16(2):107–109. https://doi.org/10.1070/MC2006v016n02ABEH002232
6. Sevostyanova N.T., Batashev S.A. Effects of the *p*-toluenesulfonic acid concentration and temperature on the combined process of dehydration and hydrocarbalcoxylation. *Byulleten' nauki i praktiki = Bulletin of Science and Practice.* 2016;7:8–13 (in Russ.). https://www.bulletennauki.ru/gallery/%D0%91%D0%9D%D0%9F%20%E2%84%967%202016.pdf
7. Sevostyanova N.T., Batashev S.A., Rodionova A.S. *One-pot* process involving dehydration of cyclohexanol and alkoxycarbonylation of cyclohexene in the presence of catalytic system $PdCl_2$–PPh_3–*p*-toluenesulfonic acid. *Russ. Chem. Bull.* 2023;72(8):1936–1939. https://doi.org/10.1007/s11172-023-3980-1
   [Original Russian Text: Sevostyanova N.T., Batashev S.A., Rodionova A.S. *One-pot* process involving dehydration of cyclohexanol and alkoxycarbonylation of cyclohexene in the presence of catalytic system $PdCl_2$–PPh_3–*p*-toluenesulfonic acid. *Izvestiya Akademii Nauk. Seriya Khimicheskaya.* 2023;72(8):1936–1939 (in Russ.).]
8. Sevostyanova N.T., Batashev S.A., Rodionova A.S. Combined process of cyclohexyl cyclohexanecarboxylate synthesis from cyclohexanol and CO catalyzed by the $Pd(OAc)_2$–PPh_3–*p*-toluenesulfonic acid system. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2023;18(1):29–37 (in Russ.). https://doi.org/10.32362/2410-6593-2023-18-1-29-37

СПИСОК ЛИТЕРАТУРЫ

1. Kalck P., Le C., Serp B.P. Recent advances in the methanol carbonylation reaction into acetic acid. *Coord. Chem. Rev.* 2020;402:213078. https://doi.org/10.1016/j.ccr.2019.213078
2. Севостьянова Н.Т., Баташев С.А. Катализаторы карбонилирования спиртов для получения карбоновых кислот и сложных эфиров (обзор). *Журн. прикладной химии.* 2022;95(8):947–970. https://doi.org/10.31857/S0044461822080011
3. Севостьянова Н.Т., Баташев С.А. Алкоксикарбонилирование ненасыщенных субстратов растительного происхождения с использованием палладиевых катализаторов как путь к получению сложноэфирных продуктов. *Катализ в промышленности.* 2023;23(1):37–55. https://doi.org/10.18412/1816-0387-2023-1-37-55
4. Liang W.-Y., Liu L., Zhou Q., Yang D., Lu Y., Liu Y. Pd-catalyzed alkoxycarbonylation of alkenes promoted by H_2O free of auxiliary acid additive. *Mol. Catal.* 2020;482:110221. https://doi.org/10.1016/j.mcat.2018.10.016
5. Eliseev O.L., Bondarenko T.N., Stepin N.N., Lapidus A.L. Carbonylation of alcohols in the $Pd(OAc)_2$/TsOH/molten salt system. *Mendeleev Commun.* 2006;16(2):107–109. https://doi.org/10.1070/MC2006v016n02ABEH002232
6. Севостьянова Н.Т., Баташев С.А. Влияние концентрации *п*-толуолсульфокислоты и температуры на совмещенный процесс дегидратации и гидрокарбалкоксилирования. *Бюллетень науки и практики.* 2016;7:8–13. https://www.bulletennauki.ru/gallery/%D0%91%D0%9D%D0%9F%20%E2%84%967%202016.pdf
7. Севостьянова Н.Т., Баташев С.А., Родионова А.С. Однореакторный совмещенный процесс дегидратации циклогексанола и алкоксикарбонилирования циклогексена в присутствии каталитической системы $PdCl_2$–PPh_3–*п*-толуолсульфокислота. *Изв. АН. Сер. хим.* 2023;72(8):1936–1939.
8. Севостьянова Н.Т., Баташев С.А., Родионова А.С. Совмещенный процесс синтеза циклогексилциклогексанкарбоксилата из циклогексанола и CO, катализируемый системой $Pd(OAc)_2$–PPh_3–*п*-толуолсульфокислота. *Тонкие химические технологии.* 2023;18(1):29–37. https://doi.org/10.32362/2410-6593-2023-18-1-29-37
9. Elks J., Ganellin C.R. (Eds.). *Dictionary of Drugs*. Boston: Springer; 1990. 2062 p. https://doi.org/10.1007/978-1-4757-2085-3
10. Herrmann N., Köhnke K., Seidensticker T. Selective product crystallization for concurrent product separation and catalyst recycling in the isomerizing methoxycarbonylation of methyl oleate. *ACS Sustainable Chem. Eng.* 2020;8(29):10633–10638. https://doi.org/10.1021/acssuschemeng.0c03432

9. Elks J., Ganellin C.R. (Eds.). *Dictionary of Drugs*. Boston: Springer; 1990. 2062 p. https://doi.org/10.1007/978-1-4757-2085-3
10. Herrmann N., Köhnke K., Seidensticker T. Selective product crystallization for concurrent product separation and catalyst recycling in the isomerizing methoxycarbonylation of methyl oleate. *ACS Sustainable Chem. Eng*. 2020;8(29):10633–10638. https://doi.org/10.1021/acssuschemeng.0c03432
11. Roesle P., Stempfle F., Hess S.K., Zimmerer J., Río Bártulos C., Lepetit B., Eckert A., Kroth P.G., Mecking S. Synthetic Polyester from Algae Oil. *Angew. Chem. Int. Ed.* 2014;53(26):6800–6804. https://doi.org/10.1002/anie.201403991
12. Quinzler D., Mecking S. Linear semicrystalline polyesters from fatty acids by complete feedstock molecule utilization. *Angew. Chem*. 2010;122(25):4402–4404. https://doi.org/10.1002/ange.201001510
13. Stempfle F., Ritter B.S., Mülhaupt R., Mecking S. Long-chain aliphatic polyesters from plant oils for injection molding, film extrusion and electrospinning. *Green Chem*. 2014;16(4):2008−2014. https://doi.org/10.1039/C4GC00114A
14. Dong K., Sang R., Wei Z., Liu J., Dühren R., Spannenberg A., Jiao H., Neumann H., Jackstell R., Franke R., Beller M. Cooperative catalytic methoxycarbonylation of alkenes: uncovering the role of palladium complexes with hemilabile ligands. *Chem. Sci.* 2018;9(9):2510–2516. https://doi.org/10.1039/C7SC02964K
15. Yang J., Liu J., Ge Y., Huang W., Ferretti F., Neumann H., Jiao H., Franke R., Jackstell R., Beller M. Efficient palladium-catalyzed carbonylation of 1,3-dienes: selective synthesis of adipates and other aliphatic diesters. *Angew. Chem. Int. Ed.* 2021;60(17):9527–9533. https://doi.org/10.1002/anie.202015329
16. Stempfle F., Quinzler D., Heckler I., Mecking S. Long-chain linear C_{19} and C_{23} monomers and polycondensates from unsaturated fatty acid esters. *Macromolecules*. 2011;44(11):4159−4166. https://doi.org/10.1021/ma200627e
17. Illner M., Schmidt M., Pogrzeba T., Urban C., Esche E., Schomaecker R., Repke J.-U. Palladium-catalyzed methoxycarbonylation of 1-dodecene in a two phase system: the path towards a continuous process. *Ind. Eng. Chem. Res.* 2018;57(27):8884–8894. https://doi.org/10.1021/acs.iecr.8b01537
18. Behr A., Vorholt A.J., Rentmeister N. Recyclable homogeneous catalyst for the hydroesterification of methyl oleate in thermomorphic solvent systems. *Chem. Eng. Sci.* 2013;99:38–43. https://doi.org/10.1016/j.ces.2013.05.040
19. Nifant'ev I.E., Sevostyanova N.T., Averyanov V.A., Batashev S.A., Vorobiev A.A., Toloraya S.A., Bagrov V.V., Tavtorkin A.N. The concentration effects of reactants and components in the $Pd(OAc)_2$/*p*-toluenesulfonic acid/trans-2,3-bis(diphenylphosphinomethyl)-norbornane catalytic system on the rate of cyclohexene hydrocarbomethoxylation. *Appl. Catal. A.: Gen.* 2012;449:145–152. https://doi.org/10.1016/j.apcata.2012.09.020
20. Vavasori A., Toniolo L., Cavinato G. Hydroesterification of cyclohexene using the complex $Pd(PPh_3)_2(TsO)_2$ as catalyst precursor. Effect of a hydrogen source (TsOH, H_2O) on the TOF and a kinetic study (TsOH: *p*-toluenesulfonic acid). *J. Mol. Catal. A: Chem.* 2003;191(1):9–21. https://doi.org/10.1016/S1381-1169(02)00358-8
21. Aver'yanov V.A., Sevost'yanova N.T., Batashev S.A. Kinetics of cyclohexene hydrocarbalkoxylation with cyclohexanol catalyzed by the $Pd(PPh_3)_2Cl_2$–PPh_3–*p*-toluenesulfonic acid system. *Pet. Chem.* 2008;48(4):287–295. https://doi.org/10.1134/S0965544108040063
    [Original Russian Text: Aver'yanov V.A., Sevost'yanova N.T., Batashev S.A. Kinetics of cyclohexene hydrocarbalkoxylation with cyclohexanol catalyzed by the $Pd(PPh_3)_2Cl_2$–PPh_3–*p*-toluenesulfonic acid system. *Neftekhimiya.* 2008;48(4):286–294 (in Russ.).]

11. Roesle P., Stempfle F., Hess S.K., Zimmerer J., Río Bártulos C., Lepetit B., Eckert A., Kroth P.G., Mecking S. Synthetic polyester from algae oil. *Angew. Chem. Int. Ed.* 2014;53(26):6800–6804. https://doi.org/10.1002/anie.201403991
12. Quinzler D., Mecking S. Linear semicrystalline polyesters from fatty acids by complete feedstock molecule utilization. *Angew. Chem*. 2010;122(25):4402–4404. https://doi.org/10.1002/ange.201001510
13. Stempfle F., Ritter B.S., Mülhaupt R., Mecking S. Long-chain aliphatic polyesters from plant oils for injection molding, film extrusion and electrospinning. *Green Chem*. 2014;16(4):2008−2014. https://doi.org/10.1039/C4GC00114A
14. Dong K., Sang R., Wei Z., Liu J., Dühren R., Spannenberg A., Jiao H., Neumann H., Jackstell R., Franke R., Beller M. Cooperative catalytic methoxycarbonylation of alkenes: uncovering the role of palladium complexes with hemilabile ligands. *Chem. Sci.* 2018;9(9):2510–2516. https://doi.org/10.1039/C7SC02964K
15. Yang J., Liu J., Ge Y., Huang W., Ferretti F., Neumann H., Jiao H., Franke R., Jackstell R., Beller M. Efficient palladium-catalyzed carbonylation of 1,3-dienes: selective synthesis of adipates and other aliphatic diesters. *Angew. Chem. Int. Ed.* 2021;60(17):9527–9533. https://doi.org/10.1002/anie.202015329
16. Stempfle F., Quinzler D., Heckler I., Mecking S. Long-chain linear C_{19} and C_{23} monomers and polycondensates from unsaturated fatty acid esters. *Macromolecules*. 2011;44(11):4159−4166. https://doi.org/10.1021/ma200627e
17. Illner M., Schmidt M., Pogrzeba T., Urban C., Esche E., Schomaecker R., Repke J.-U. Palladium-catalyzed methoxycarbonylation of 1-dodecene in a two phase system: the path towards a continuous process. *Ind. Eng. Chem. Res.* 2018;57(27):8884–8894. https://doi.org/10.1021/acs.iecr.8b01537
18. Behr A., Vorholt A.J., Rentmeister N. Recyclable homogeneous catalyst for the hydroesterification of methyl oleate in thermomorphic solvent systems. *Chem. Eng. Sci.* 2013;99:38–43. https://doi.org/10.1016/j.ces.2013.05.040
19. Nifant'ev I.E., Sevostyanova N.T., Averyanov V.A., Batashev S.A., Vorobiev A.A., Toloraya S.A., Bagrov V.V., Tavtorkin A.N. The concentration effects of reactants and components in the $Pd(OAc)_2$/*p*-toluenesulfonic acid/trans-2,3-bis(diphenylphosphinomethyl)-norbornane catalytic system on the rate of cyclohexene hydrocarbomethoxylation. *Appl. Catal. A.: Gen.* 2012;449:145–152. https://doi.org/10.1016/j.apcata.2012.09.020
20. Vavasori A., Toniolo L., Cavinato G. Hydroesterification of cyclohexene using the complex $Pd(PPh_3)_2(TsO)_2$ as catalyst precursor. Effect of a hydrogen source (TsOH, H_2O) on the TOF and a kinetic study (TsOH: *p*-toluenesulfonic acid). *J. Mol. Catal. A: Chem.* 2003;191(1):9–21. https://doi.org/10.1016/S1381-1169(02)00358-8
21. Аверьянов В.А., Севостьянова Н.Т., Баташев С.А. Кинетические закономерности гидрокарбоалкоксилирования циклогексена циклогексанолом, катализируемого системой $Pd(PPh_3)_2Cl_2$ – PPh_3 – *п*-толуолсульфокислота. *Нефтехимия*. 2008;48(4):286–294.
22. Аверьянов В.А., Баташев С.А., Севостьянова Н.Т., Носова Н.М. Кинетика и механизм катализируемого комплексом Pd(II) гидрокарбометоксилирования циклогексена. *Кинетика и катализ.* 2006;47(3):381–390.
23. Петров Э.С. Фосфиновые комплексы палладия в катализе реакций карбонилирования олефинов. *Журн. физ. химии.* 1988;62(10):2858–2868.
24. Белобородов В.Л., Зурабян С.Э., Лузин А.П., Тюкавкина Н.А. *Органическая химия*. М.: ГЭОТАР-Медиа; 2019. Кн. 1. 640 с.

22. Aver'yanov V.A., Batashev S.A., Sevost'yanova N.T., Nosova N.M. Kinetics and mechanism of cyclohexene hydrocarbomethoxylation catalyzed by a Pd(II) complex. *Kinet. Catal.* 2006;47(3):375–383. https://doi.org/10.1134/S0023158406030086
[Original Russian Text: Aver'yanov V.A., Batashev S.A., Sevost'yanova N.T., Nosova N.M. Kinetics and mechanism of cyclohexene hydrocarbomethoxylation catalyzed by a Pd(II) complex. *Kinetika i Kataliz.* 2006;47(3):381–390 (in Russ.).]
23. Petrov E.S. Phosphine complexes of palladium in the catalysis of olefin carbonylation reactions. *Zhurnal Fizicheskoi Khimii*. 1988;62(10):2858–2868 (in Russ.).
24. Beloborodov V.L., Zurabyan S.E., Luzin A.P., Tyukavkina N.A. *Organicheskaya khimiya* (*Organic Chemistry*). Moscow: GEOTAR-Media; 2019. V. 1. 640 p. (in Russ.).

About the authors

Nadezhda T. Sevostyanova, Cand. Sci. (Chem.), Associate Professor, Senior Researcher, Head, Research and Production Center Himreaktivdiagnostika, Tula State Lev Tolstoy Pedagogical University (125, Lenina pr., Tula, 300026, Russia). E-mail: sevostyanova.nt@gmail.com. Scopus Author ID 25643582900, ResearcherID M-8567-2014, RSCI SPIN-code 9239-7136, https://orcid.org/0000-0002-3499-2226

Sergey A. Batashev, Cand. Sci. (Chem.), Associate Professor, Senior Researcher, Research and Production Center Himreaktivdiagnostika, Tula State Lev Tolstoy Pedagogical University (125, Lenina pr., Tula, 300026, Russia). E-mail: tulapharma@gmail.com. Scopus Author ID 14071256200, ResearcherID N-1405-2018, RSCI SPIN-code 8241-9789, https://orcid.org/0000-0001-7537-7740

Anastasia S. Rodionova, Researcher, Tula State Lev Tolstoy Pedagogical University (125, Lenina pr., Tula, 300026, Russia). E-mail: rodionova.nastia@ya.ru. Scopus Author ID 57189375048, https://orcid.org/0000-0002-0896-5208

Dar'ya K. Kozlenko, Researcher, Tula State Lev Tolstoy Pedagogical University (125, Lenina pr., Tula, 300026, Russia). E-mail: dk.reshetnikova@yandex.ru. Scopus Author ID 58600613300, https://orcid.org/0009-0009-7166-8415

Об авторах

Севостьянова Надежда Тенгизовна, к.х.н., доцент, старший научный сотрудник, руководитель научно-производственного центра «Химреактивдиагностика», ФГБОУ ВО «Тульский государственный педагогический университет им. Л.Н. Толстого» (300026, Россия, г. Тула, пр-т Ленина, д. 125). E-mail: sevostyanova.nt@gmail.com. Scopus Author ID 25643582900, ResearcherID M-8567-2014, SPIN-код РИНЦ 9239-7136, https://orcid.org/0000-0002-3499-2226

Баташев Сергей Александрович, к.х.н., доцент, старший научный сотрудник научно-производственного центра «Химреактивдиагностика», ФГБОУ ВО «Тульский государственный педагогический университет им. Л.Н. Толстого» (300026, Россия, г. Тула, пр-т Ленина, д. 125). E-mail: tulapharma@gmail.com. Scopus Author ID 14071256200, ResearcherID N-1405-2018, SPIN-код РИНЦ 8241-9789, https://orcid.org/0000-0001-7537-7740

Родионова Анастасия Сергеевна, исполнитель по гражданско-правовому договору реализации гранта Российского научного фонда, ФГБОУ ВО «Тульский государственный педагогический университет им. Л.Н. Толстого» (300026, Россия, г. Тула, пр-т Ленина, д. 125). E-mail: rodionova.nastia@ya.ru. Scopus Author ID 57189375048, https://orcid.org/0000-0002-0896-5208

Козленко Дарья Константиновна, исполнитель по гражданско-правовому договору реализации гранта Российского научного фонда, ФГБОУ ВО «Тульский государственный педагогический университет им. Л.Н. Толстого» (300026, Россия, г. Тула, пр-т Ленина, д. 125). E-mail: dk.reshetnikova@yandex.ru. Scopus Author ID 58600613300, https://orcid.org/0009-0009-7166-8415

Translated from Russian into English by V. Glyanchenko
Edited for English language and spelling by Dr. David Mossop