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ESTABLISHING OPTIMAL CONDITIONS FOR CATALYTIC OBTAINING OF ALLYL-1,3,4-TRIMETHYLCYCLOHEX-3-ENCARBOXYLATE

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Досліджена кінетика реакції каталітичного циклоприєднання 2,3-диметилбута-1,3-дієну і алілметакрилату за реакцією Дільса-Альдера. Визначені константи швидкості і активаційні параметри реакції. Досліджено вплив температури, молярного співвідношення реагентів і каталізатора на вихід цільового продукту. Встановлені оптимальні умови каталітичного одержання аліл-1,3,4-триметилциклогекс-3-енкарбоксилату

***Ключові слова:** 2,3-диметилбута-1,3-дієн, алілметакрилат, аліл-1,3,4-триметилциклогекс-3-енкарбоксилат, реакція Дільса-Альдера*

Исследована кинетика реакции каталитического циклоприсоединения 2,3-диметилбута-1,3-диена и аллилметакрилата по реакции Дильса-Альдера. Определены константы скорости и активационные параметры реакции. Исследовано влияние температуры, молярного соотношения реагентов и катализатора на выход целевого продукта. Установлены оптимальные условия каталитического получения аллил-1,3,4-триметилциклогекс-3-енкарбоксилата

***Ключевые слова:** 2,3-диметилбута-1,3-диен, аллилметакрилат, аллил-1,3,4-триметилциклогекс-3-енкарбоксилат, реакция Дильса-Альдера*

1. Introduction

Esters of alkyl cyclohexane carbonic acids, as products of organic synthesis, belong to an inadequately studied class of substances. Published information on the methods of synthesis, chemical properties and areas of application are practically absent and relate mainly to saturated derivatives of cyclohexene carbonic acids. Besides, esters of alkylcyclohexenecarbonic acids are raw materials for preparation of food flavors, perfumery compositions, plasticizers, comonomers, plant growth regulators, drugs and hydro-aromatic hydrocarbons.

Alkyl cyclohexene compounds are increasingly being used as monomers in production of new polymeric materials. Alkylcyclohexenecarboxylates are the basis for synthesis of polyfunctional polymers of diverse structures with a predefined set of physical-chemical characteristics [1].

Availability of homologous series creates a practical possibility of synthesis of secondary, tertiary and hydro-aromatic hydrocarbons and production of perfumery compositions [2]. Much of the esters of alkylcyclohexenecarbonic acids are structural fragments of vitamins, hormones and alkaloids.

The problem of developing catalytic processes for production of esters of alkylcyclohexenecarbonic acids is relevant at present. The search for new substances makes it possible to expand the range of materials with better and varied properties to meet growing needs of science and technology.

Catalytic production of esters of alkylcyclohexenecarbonic acids by the Diels-Alder reaction has not only theoretical but also practical value. No by-products are formed during their synthesis and the process is effective and appropriate for production of both saturated and unsaturated esters of alkylcyclohexenecarbonic acids.

Use of the reaction of [4+2]-cyclic addition of 2.3-dimethylbuta-1,3-diene (DMB) with the corresponding unsaturated esters enables production of new esters of alkylcyclohexenecarbonic acids at high yields. Therefore, the most promising from the technological point of view is the method of obtaining esters of alkylcyclohexenecarbonic acids by the catalytic Diels-Alder reaction due to the virtually complete conversion of the starting reagents and absence of side reactions.

2. Literature review and problem statement

To date, esters of alkylcyclohexenecarbonic acids are obtained by methods of esterification, oxidation of cyclocarbaldehydes, cyclic addition of dienes and dienophiles by the Diels-Alder reaction. The most suitable for both laboratory practice and industrial production is synthesis of esters of alkylcyclohexenecarbonic acids by the Diels-Alder reaction. Compared to other methods, it is based on accessible raw materials, enables high yields of target products, has a much shorter process time and is safer and easier hardware implementation.

The ability of the diene synthesis to be activated at lower temperatures under the influence of certain additives is presented in [3–5].

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The reaction of DMB with γ, γ, γ-trichlorcrotonol aldehyde occurs under thermal conditions with formation of a cyclohexane derivative with a yield of 84 % and in presence of aluminum chloride, up to formation of a dihydropyran series (with simultaneous allyl regrouping) [3] (Fig. 1).

In the presence of catalysts, diene synthesis proceeds structurally and more selectively [4]. The ratio of para- and meta-adducts in thermal synthesis of isoprene with methyl acrylate is 70:30 and in the reaction which is catalyzed by aluminum chloride, this ratio reaches 95:5 (Fig. 2).

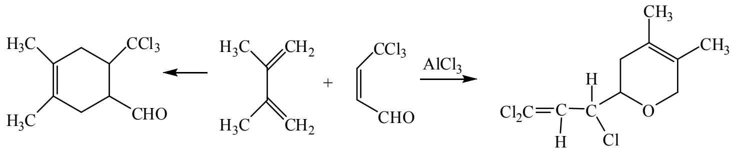


Fig. 1. Reaction of interaction of DMB and γ, γ, γ-trichloroctonic aldehyde

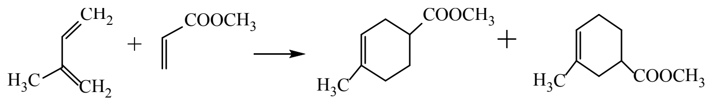


Fig. 2. Reaction of interaction of isoprene and methacrylate

The magnitude of the difference in the rates of non-catalyzed and catalyzed reactions as well as influence of a substituent in diene on the rate of extraction [4], make it possible to consider the catalyzed reactions according to a two-stage heterolytic mechanism. Its rate is determined by the rate of the stage of the electrophilic attack of the β-carbon atom of the dienophile coordinated by the catalyst [4]. The fact of formation of complexes with the Lewis acids with polar groups of dienophiles was confirmed by infrared spectra [5]. Kinetic studies of the catalyzed reaction of butadiene with methyl acrylate have shown that concentration of methyl acrylate in the reaction mixture can be varied with respect to the aluminum chloride concentration in the range of 1.7–42 times, without much effect on the conversion rate which, in turn, is proportional to the catalyst concentration. This fact indicates that the true reagent is a complex of methyl acrylate with aluminum chloride. Thus, the general scheme can be considered by the following equation (Fig. 3).

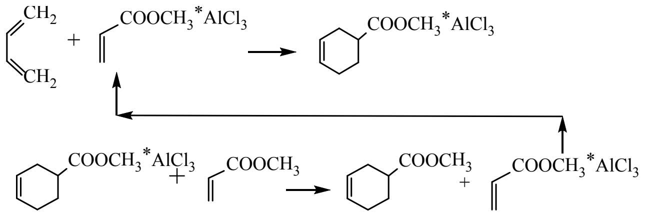


Fig. 3. Catalytic interaction of butadiene and methacrylate

The kinetic expression of its rate is determined by the equation:

$$\text{rate}=k\cdot[\text{butadiene}]\cdot[\text{methyl acrylate AlCl}_3].$$

For the catalyzed and non-catalyzed reactions of butadiene with methyl acrylate, the values of activation energy were determined: $E_{cat}=43.5\pm7.9$ and $E=75.3\pm4.2$ kJ/mol, respectively, and the pre-exponential factor $\lg A_{cat}=4.8\pm1.4$ and $\lg A=5.4\pm0.6$ (s^{-1}). The difference in the rate constants of catalyzed and non-catalyzed reactions is 10^5 times. The proximity of the Arrhenius factors in both reactions indicates that they occur with a strictly limited spatial arrangement of the addends [5–8].

Mesoporous silicon nanoparticles were used for the Diels-Alder reaction [9]. The study was conducted for reactions of interaction of cyclopentadiene with acrolein, methacrolein and methylmetacrolein. Mesoporous silicon nanoparticles were used in three samples with 50, 100 and 150 nm nanoparticles, respectively.

During interaction of cyclopentadiene with acrolein without catalyst, the product yield was 62.5 % and the process was carried out at 353 K. The first sample of catalyst with the size of mesoporous silicon nanoparticles (MSN) of 50 nm has made it possible to reduce the process temperature to 313 K and achieve an 84.9 % yield of the product. The second sample with a nanoparticle size of 100 nm increased the product yield to 93.1 %. Use of the third sample with a nanoparticle size of 150 nm allowed us to reach 86.9 % yield of the target product. The process rate constant without a catalyst was $5\cdot10^{-3}$ s^{-1} and when a sample with nanoparticle size of 100 nm was used, the rate increased to 1.71 s^{-1}.

A similar trend was observed for the reaction of cyclopentadiene with methacrolein. When the reaction occurred without catalyst, the product yield was 45.5 %. The first example of the catalyst allowed us to increase the yield to 81.6 %, the second to 95.3 %, and the third to 96.7 %. The process rate constant without catalyst was $4.7\cdot10^{-3}$ s^{-1} and when a sample with a nanoparticle size of 100 nm was used, the rate increased to 1.67 s^{-1}.

When cyclopentadiene interacted with methyl methacrolein without catalyst, the authors obtained only 7.7 % of the product. When the first sample was used, the product yield increased to 23 %. The second sample of the catalyst enabled product yield of 67.2 % and the third sample of the catalyst increased the product yield to 34 %. The process rate constant without catalyst was $4.2\cdot10^{-3}$ s^{-1} and when using a sample with nanoparticle size of 100 nm, it increased to 1.66 s^{-1}.

It was determined that the optimum size of mesoporous silicon nanoparticles is 100 nm since it is precisely when using the second sample, the products yield reached maximum values. Besides, the authors found that the catalytic activity of silicon nanoparticles significantly increased the reaction rate constants.

Silver nanoparticles were used in work [10] as a catalyst for the Diels-Alder diene synthesis assuming that the nanocatalysis proceeds according to the following scheme (Fig. 4).

To elucidate catalytic action of silver nanoparticles, the authors conducted kinetic studies of interaction of DMB with 2-hydroxyhalcone without catalyst and in the presence of silver nanoparticles. One equivalent of 2-hydroxyhalcone and 22 equivalents of DMB were used for the study. Due to the use of nanocatalyst in an amount of 0.25 % of the content of the entire mixture, the authors managed to reduce the process temperature from 423 K to 313 K and essentially reduce the interaction time. When using nanocatalyst, the reaction time reduced to 5 hours whereas without it duration of the process was 36 hours. In addition, the product yield increased to 95 % while it did not exceed 85 % in non-catalytic conditions. The rate constant of the catalytic reaction was $3.6\cdot10^{-2}$ l/mol·s.

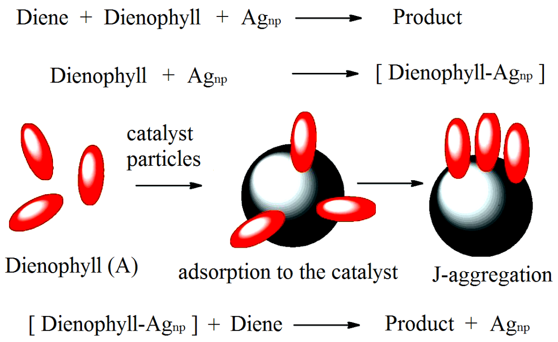


Fig. 4. Mechanism of catalytic interaction of DMB with 2-hydroxyhalcone

Silver nanoparticles deposited on silicon surface were also used in [10]. The studies were carried out for the reaction of [4+2]-cyclic addition (0.01 mmol) of 1 equivalent of 2-hydroxyhalcone and (0.4 mmol) of 4 equivalents of 1-phenyl-3-methylbutadiene. Use of nanocatalysts in an amount of 0.2 % of the entire mixture content has allowed us to reduce the process temperature from 323 K to 298 K and significantly reduce the interaction time. When using nanocatalyst, reaction time decreased to 5 hours whereas without it duration of the process was 48 hours. In addition, the product output increased to 96 % while in non-catalytic conditions it was 88 %. The rate constant of the catalytic reaction was $3.8\cdot10^{-2}$ l/mol·s.

In [11], tungsten-phosphoric heteropolic acid ($H_3PW_{12}O_{40}$) applied to the surface of silica gel was used as a catalyst for the Diels-Alder reactions. The reaction of interaction of isoprene with acrolein with addition of 0.49 % mol of $H_3PW_{12}O_{40}$ applied to the surface of silica gel enabled attainment of a 54 % product yield during 7 hours at 293 K. At 0.47 % mol of $H_3PW_{12}O_{40}$, a 63 % product yield was achieved during 8 hours at 273 K.

The authors of [11] also investigated reaction of interaction of DMB with acrolein. When 0.49 % mol. catalyst was added for 5 hours at 273 K, they managed to achieve a 78 % product yield.

In addition, they investigated in more detail reaction of interaction of 1,3-cyclohexadiene with acrolein. The results obtained by the authors indicate that increase in the amount of $H_3PW_{12}O_{40}$ catalyst significantly reduced reaction time and increased product yield. For example, with addition of 0.092 % mol catalyst to the reaction mixture, interaction occurred in 8 hours at 273 K with a yield of 60 %. Respective figures were 7 hours at 293 K with a yield of 75 % for 0.098 % mol catalyst and 4 hours at 273 K with a yield of 94 % for 0.48 % mol catalyst.

Studies of interaction of cyclopentadiene with 3-menthyl-methylacrylate and 3-menthyl- acrylate were carried out and presented in [12]. For catalysis of this process, BBr_3 was used. Use of 0.25 % mol of BBr_3 has made it possible to change the reaction temperature by 283 K from 273 to 353 K with the product yield varying from 38 % to 58 %, respectively.

An asymmetric interaction of 1,3-butadienes with dimethyl fumarate was investigated in [13]. As a catalyst, BBr_3 and BBr_3-$O(C_2H_5)_2$ were used. When using the BBr_3 catalyst in an amount of 0.5 % mol, the process temperature was 263 K and the yield of the product reached 38 %. While BBr3-O(C_2H_5)$_2$ was used in an amount of 0.25 % mol, the process temperature was also 263 K and the product yield did not exceed 23 %. In addition, to carry out these processes, the reaction had to be carried out in a medium of dichloromethane solvent.

With the use of BBr_3-$C_{10}H_{20}O$-OC_2H_5 catalyst, catalytic interaction of cyclopentadiene with propyl acrylate occurred in a dichloromethane medium [14]. In the case of using this catalyst (0.25 % mol), the process temperature was 203 K and the target product yield reached 85 %.

The study of reaction of interaction of diethyl azodicarboxylate with unsaturated fatty acids was carried out in [15]. The authors investigated influence of the system of solvent and catalysts. For the study of the catalytic action of trifluoroacetate and trichloracetate acids, reaction of [4+2]-cyclic addition of diethyl azocarboxylate and unsaturated fatty acids was carried out in a gasoline medium. The use of trifluoroacetate and trichloro acetate acid has made it possible to reduce the process temperature from 386 K to 313–323 K. Yield of the target product with the use of catalyst (trifluoroacetate acid) increased to 82 %, reaction rate constant was $3.6\cdot10^{-3}$ l/mol·s at 313 K, and $7.5\cdot10^{-3}$ l/mol·s at 323 K. Using a catalyst (trichloro acetate acid), the product yield increased to 79 %; the reaction rate constant was $3.5\cdot10^{-3}$ l/mol·s at 313 K, and $5.2\cdot10^{-3}$ l/mol·s at 323 K, respectively.

In [16], catalysis [4+2]-cyclic addition of 1,3-dienes and acrylates (aluminum enriched with mesoporous alumosilicate) was used.

For example, in interaction of 1 mol of methyl acrylate and 3 mol of DMB in a medium of *n*-hexane, the use of the hexagonal mesoporous Al-Si enabled reaction at 272 K during 8 hours with a 96 % yield of the target product. The authors also investigated interaction of 3 mol of isoprene and 1 mmol of methyl methacrylate in a medium of *n*-hexane. The temperature of the process was 272 K, the product yield did not exceed 87 %.

Interaction of isoprene and methyl vinyl ketone with the possibility of using the catalytic action of zeolites was studied in [17]. For this study, authors selected three zeolites, namely zeolites of grades Y, EMT, and BET. The use of Y and EMT zeolites did not show any positive changes in the process while the BET zeolite has made it possible to reduce the reaction temperature to 273 K and duration to 5 hours.

The study of action of the catalytic systems of N-hexylpyridinium bis(trifluoromethylsulfonyl)-imide and the Lewis acids (YCl_3, $YbCl_3$, $MgCl_2$, $ZnCl_2$) on the Diels-Alder reactions are presented in [18]. Catalytic systems were used for interactions of cyclopentadiene with ethyl acrylate, methyl vinyl ketone and dimethyl maleate. Catalytic systems have made it possible to lower the process temperature to a range of 293–318 K. In interaction of cyclopentadiene and ethyl acrylate, optimum temperature of the catalytic reaction was 308 K. Activation energy was 40.6 kJ/mole and the constant of the reaction rate was $2.58\cdot10^{-5}$ l/mol·s. Yield of the target product in these conditions reached 90 %.

Catalysis of the reaction [4+2]-cyclic addition of 2,3-dimethylbut-1,3-diene and benzaldehydes using montmorillonite was carried out in [19]. The use of this catalyst has made it possible to reduce temperature of interaction from 383 K to 298 K. When DMB was interacting with benzaldehyde, o-bromobenzaldehyde, o-nitro benzaldehyde for 1 hour at 298 K, the product yield was 52 %, 68 %, 75 %, respectively. In the case of [4+2]-cyclic addition of DMB and p-chlorobenzaldehyde, interaction took place for 24 minutes, the product yield was 56 % and in interaction of DMB and o-fluor benzaldehyde during 15 minutes, the product yield was 49 %.

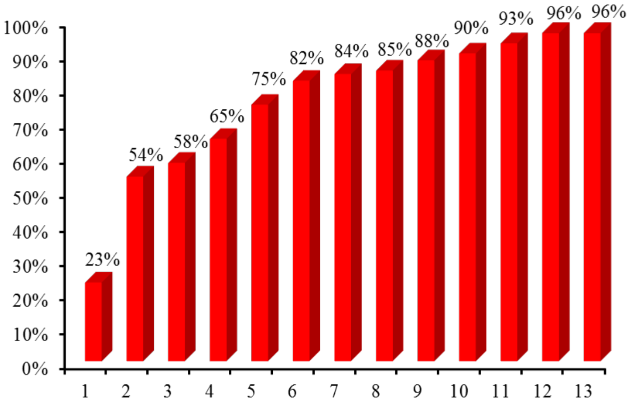


Fig. 5. Dependence of the yield of esters of alkylcyclohexenecarbonic acids on the nature of the catalyst: BBr_3*O $(C_2H_5)_2$ catalyst [13] (No. 1); $H_3PW_{12}O_{40}$ catalyst applied to the surface of silica gel [11] (No. 2); BBr_3 catalyst [13] (No. 3); zeolite BET catalyst [17] (No. 4); montmorillonite catalyst [19] (No. 5); trifluoracetic acid as catalyst [15] (No. 6); Al_2O_3 catalyst [4] (No. 7); $BBr_2O\text{-}C_{10}H_{20}O\text{-}OC_2H_5$ catalyst [14] (No. 8); $BBr_2O\text{-}C_{10}H_{20}O$ catalyst [14] (No. 9); N-hexylpyridinium catalyst [18] (No. 10); 100 nm size mesoporous silicon particles as catalyst [9] (No. 11); hexagonal mesoporous Al-Si catalyst [16] (No. 12); Ag nanoparticle powder catalyst [10] (No. 13)

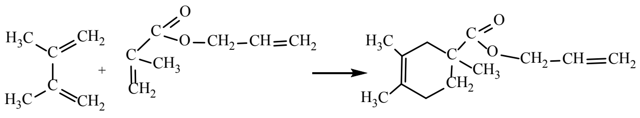
To conclude, analysis of the data presented in Fig. 5 shows that the authors managed to achieve best results in the use of silicon and silver nanoparticles as well as hexagonal mesoporous Al-Si. In addition, $H_3PW_{12}O_{40}$ was also an effective catalyst. It is also indicated that not only the nature of the catalyst affects the reaction rate and yield of the target product but also the size of the catalyst nanoparticles.

When using most catalysts, the authors managed not only to increase yield of target products but also conduct the process at atmospheric pressure, significantly reduce the process temperature and reduce reaction time. It is worth noting that classical catalysts such as the Lewis acids are not sufficiently effective compared to the nanocatalysts. The use of silver nanoparticles for catalysis of the Diels-Alder processes has allowed the authors to reduce temperature by almost half and shorten the interaction time from 36 to 5 hours. At the same time, it was possible to achieve a 96 % yield of the target product in contrast to 85 % in non-catalyzed conditions [10].

Since there is so little information about the use of metal nanoparticles in the diene Diels-Alder synthesis, the mechanism of such reactions is not sufficiently studied to the moment. Therefore, in order to determine the effect of nanocatalysis on the reactions under study, it was necessary to conduct a series of relevant experiments described in this paper.

3. The aim and objectives of the study

This study objective was to develop a selective process for the preparation of allyl-1,3,4-trimethylcyclohex-3-enecarboxylate.



To achieve this objective, it was necessary to solve the following tasks:

1) investigate influence of temperature, molar ratio of reagents and catalyst per yield of the target product;

2) investigate kinetic regularities of the catalytic reactions of [4+2]-cyclic addition of 2,3-dimethylbuta-1,3-diene and esters of acrylic acids and determine the order of reaction and the energy parameters on their basis;

3) propose ways of practical application of esters of alkyl cyclohexene carbonic acids.

4. The procedure for catalytic production of allyl-1,3,4-trimethylcyclohex-3-enecarboxylate

Allyl methacrylate of “kh.ch.” brand and 2,3-dimethylbuta-1,3-diene previously obtained by us in accordance with [20] were used for synthesis.

Allyl methacrylate and 2,3-dimethylbuta-1,3-diene at a molar ratio of 1:4 and 0.25 % mol of $Ag_{n.p.}$, fine-disperse silver, in a form of 10 nm nanoparticles were charged in the reactor equipped with a casing to provide heating. Stirring was carried out using a magnetic stirrer. The studies were carried out in a temperature range of 303–333 K. After a period of time, samples were taken from the reactor and the reaction mixture was analyzed by gas-liquid chromatography using SELMI CHROM-1 with a computer data logging [21].

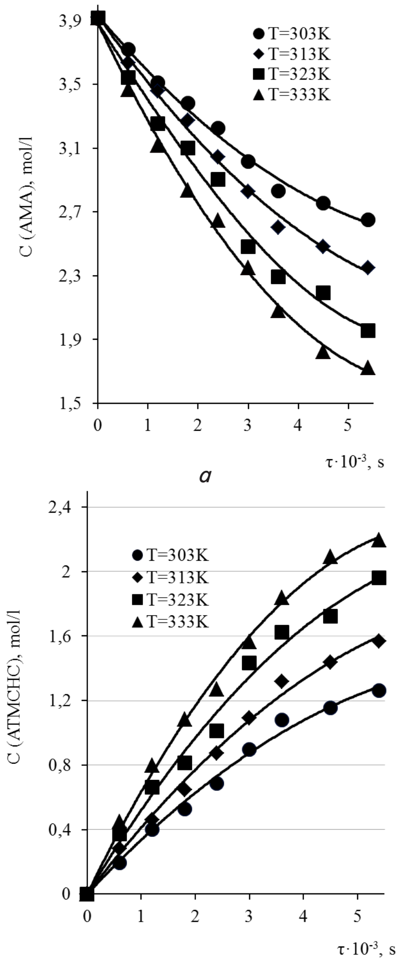
Quantitative analysis was carried out by the method of internal normalization. Error of the chromatographic analysis did not exceed 3 % [22].

5. The results obtained in the study of reaction of catalytic cyclic addition of 2,3dimethylbuta-1,3-diene and allyl methacrylate by the Diels-Alder reaction

The kinetic curves of consumption of allyl methacrylate and their anamorphoses are shown in Fig. 6, *a, b*, and accumulation of allyl-1,3,4-trimethylcyclohex-3-enecarboxylate (ATMCHC) is shown in Fig. 3. Kinetic studies have established that the catalytic interaction of 2,3-dimethylbuta-1,3-diene (DMB) and allyl methacrylate (AMA) at a 4:1 molar ratio in the initial sections of the curves (Fig. 6, 7) is satisfactorily described by the kinetic equation of irreversible second-order reactions. This corresponds to the published data for the relevant reactions [23].

Since the kinetic studies were carried out at a ratio DMB:AMA=4:1, the least squares method was used to process experimental data. We used the dependence $(1/[C_1]_o-[C_2]_o)\times$ $\times\ln([C_1]_t\cdot[C_2]_o/[C_1]_o\cdot[C_2]_t)=k\cdot t$ [24] for the second-order anamorphoses with a non-equivalent ratio of reagents. Constants of the reaction rate were determined by the nature of dependence of the tangent of the angle of inclination of the kinetic curves (Table 1).

From the data shown in Table 1, it is obvious that the values of the second-order constants increase with increase in temperature of [4+2]-cyclic addition of DMB and AMA. It is known that the dependence of the rate constants on temperature is described by the Arrhenius equation. This allows one to determine activation energy and other activation parameters of the process of ATMCHC production.



a

b

Fig. 6. Graphic results of kinetic studies: kinetic curves of consumption of allyl methacrylate (AMA) in the reaction of [4+2]-cyclic addition at 303–333 K and molar ratio DMB:AMA=4:1, catalyst: $Ag_{n.p.}$ (0.25 % mol) (*a*) anamorphoses in the reaction of [4+2]-cyclic addition at 303-333 K and molar ratio DMB:AMA=4:1, catalyst: $Ag_{n.p.}$ (0.25 % mol) (*b*)

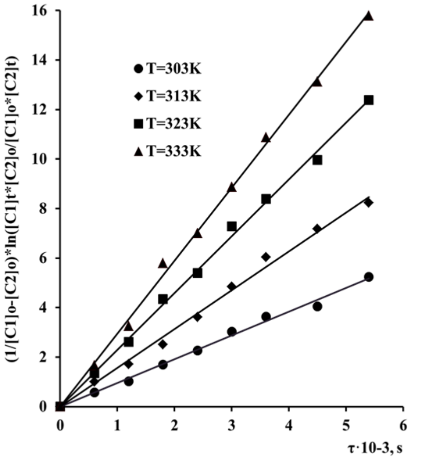


Fig. 7. Kinetic curves of ATMCHC accumulation

Table 1

Dependence of constants of the rate of [4+2]-cyclic addition of DMB and AMA from temperature at molar ratio DMB:AMA=4:1, catalyst: $Ag_{n.p.}$ (0.25 % mol)

Temperature, K	$(k \pm \Delta k) \cdot 10^3$, l/(mol·s)	AMA conversion, %
303	0.9±0.1	33
313	1.6±0.2	40
323	2.3±0.3	50
333	2.9±0.5	57

The correlation coefficient is satisfactory ($R^2>0.98$). Fig. 8 shows the dependence of the constant of the reaction rate on temperature in the coordinates of the Arrhenius equation.

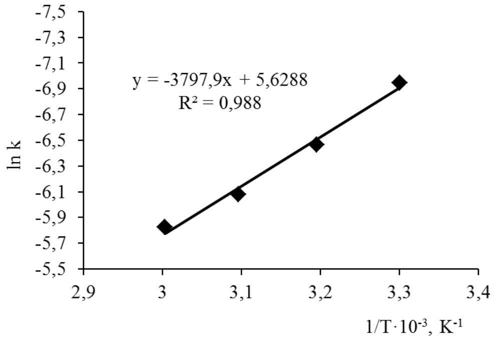


Fig. 8. Dependence of the rate constant of reaction of [4+2]-cyclic addition of DMB and AMA from temperature; catalyst: $Ag_{n.p.}$ (0.25 % mol)

From the shown dependence (Fig. 8), activation energy was determined. Thermodynamic parameters of the activation state: the change of enthalpy ΔH and the change of entropy ΔS were calculated according to the Eyring equation [24] (Table 2).

Table 2

Activation parameters of reaction of [4+2]-cyclic addition of DMB and AMA; catalyst: $Ag_{n.p.}$ (0.25 % mol)

$E \pm \Delta E$, kJ/mol	ΔH, kJ/mol	ΔS, J/mol·K	A, l/(mol·s)
32.6±1.3	30.0	−203.7	$1.0 \cdot 10^6$

Activation energy of catalytic production of ATMCHC is E_{act}=32.6 kJ/mol. This indicates that under the studied experimental conditions, the energy barrier of [4+2]-cyclic addition of DMB and AMA is almost halved compared to the activation energy of the non-catalytic production of ATMCHC, E_{act}=76.6 kJ/mol [23].

The high negative value of the change in the activation entropy in production of ATMCHC ΔS=–203.7 J/(mol·K) of the process of catalytic [4+2]-cyclic addition and the value of enthalpy of the activated state of ATMCHC ΔH=30.0 kJ/mol is characteristic of the Diels-Alder reactions [24]. Discontinuity and formation of bonds are synchronous and energy consumption for the discontinuity of one bond in the transition state is compensated by the energy of formation of another one [24]. The investigated reaction is energy beneficial.

On the basis of the obtained rate constants and the activation parameters of the catalytic [4+2]-cyclic addition of DMB and AMA, it was found that the reaction under investigation is subject to a second-order kinetic law. Thus, in the temperature range of 303–333 K with the use of $Ag_{n.p.}$, the reaction of obtaining esters of alkyl cyclohexenecarbonic acids proceeds with a satisfactory rate when AMA conversion becomes sufficiently high.

Table 3 shows main characteristics of the $Ag_{n.p.}$ catalyst (0.25 % mol).

Table 3

Main characteristics of the $Ag_{n.p.}$ catalyst (0.25 % mol)

Catalytic activity, A	Energy effect, kJ/mol	Catalyst activation temperature, K
197	44.0	333

Catalytic activity indicates the number of active centers involved in the catalytic process and accordingly determines the maximum number of molecules reacted at one active center per unit time. In addition, expediency of using the $Ag_{n.p.}$ catalyst is confirmed by the values of its energy effect and the catalyst activation temperature. This enables the reaction of [4+2]-cyclic addittion at a rather low temperature of 333 K and atmospheric pressure.

Based on the results obtained, it can be asserted that the use of catalysts can increase the rate of reaction of obtaining esters of alkylcyclohexenecarbonic acids and significantly reduce the energy barrier. Lowering of the activation energy enables [4+2]-cyclic addition of DMB and AMA at catalyst activation temperature of 333 K while it is required to ensure 433 K at a noncatalyzed process [23].

On the basis of the studied kinetic regularities, influence of temperature, molar ratio of reagents and the catalyst on the yield of the target product was investigated.

To elucidate the effect of temperature of catalytic [4+2]-cyclic addition of DMB and AMA, study was conducted in the temperature range of 303–333 K at a molar ratio DMB:AMA=4:1 and with participation of $Ag_{n.p.}$ catalyst (0.25 % mol, with particle size of 10 nm). As a result of the conducted studies, data were obtained that characterize temperature effect on the yield of ATMCHC in the catalytic [4+2]-cyclic addition of DMB and AMA.

With an increase in temperature from 303 to 333 K, ATMCHC yield increases from 58 % to 76 %. With further increase in temperature, DMB boils, and AMA remains in liquid state, accordingly it is not worth to expect significant increase in the the target product yield. In addition, temperatures higher than 333 K are not relevant for the catalytic process.

Fig. 9 shows the dependence of ATMCHC yield on the temperature of catalytic [4+2]-cyclic addition of DMB and AMA.

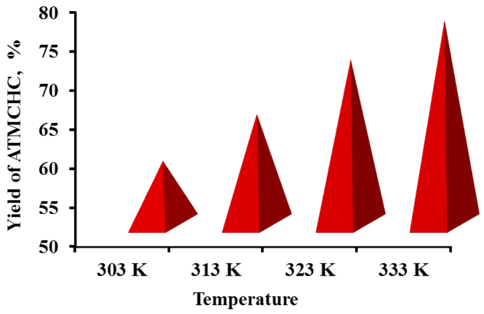


Fig. 9. Influence of temperature on ATMCHC yield at molar ratio DMB:AMA=4:1 in presence of $Ag_{n.p.}$ catalyst (0.25% mol)

From the data obtained in the catalytic process of [4+2]-cyclic addition of DMB and AMA, an optimal temperature interval of 323–333 K was chosen since it provides maximum output of ATMCHC (Fig. 9).

The molar ratios were studied in the range of DMB: AMA=1.5:1; 2:1; 3:1, 4:1, 5:1, 6:1. The data obtained in the studies characterize effect of the molar ratio of reagents on ATMCHC yield during catalytic [4+2]-cyclic addition of DMB and AMA.

The dependence of ATMCHC yield on the molar ratio of reagents DMB:AMA in the presence of $Ag_{n.p.}$ catalyst is shown in Fig. 10.

With an increase in the excess of DMB:AMA from 1.5:1 to 4:1, ATMCHC yield increases from 54 % to 76 %. With further increase in DMB excess, there is no significant increase in ATMCHC yield. In addition, the use of a large excess is unprofitable in an industrial scale.

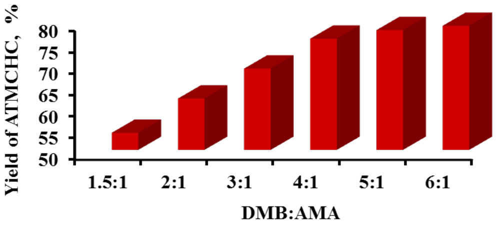


Fig. 10. Influence of the molar ratio of DMB:AMA on ATMCHC yield at 333 K in the presence of $Ag_{n.p.}$ catalyst (0.25 % mol)

The optimal molar ratio of reagents in catalytic [4+2]-cyclic addition of DMB and AMA is DMB:AMA=4:1 since as it can be seen from Fig. 10, it is precisely at this ratio that the maximum ATMCHC yield is achieved.

The following catalysts were used to study the catalytic action on ATMCHC yield: $Ag_{n.p.}$, $Pd_{n.p.}$, $Au_{n.p.}$, Cu_2Cl_2. Investigation of the catalyst effect was carried out at a temperature of 333 K and a molar ratio of DMB:AMA=4:1.

As a result of the studies, data were obtained that characterize the effect of catalysts on ATMCHC yield in [4+2]-cyclic addition of DMB and AMA.

The best indicators of ATMCHC yield were obtained with the use of $Ag_{n.p.}$ catalyst. i. e. 76 %. Somewhat lower yields were obtained with $Pd_{n.p.}$, $Au_{n.p.}$, Cu_2Cl_2.

Fig. 11 shows dependence of ATMCHC yield on the catalyst nature.

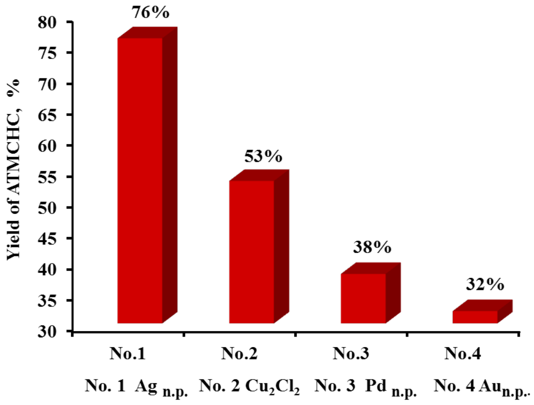


Fig. 11. Effect of the catalyst nature (0.25 % mol) on ATMCHC yield at 333 K and the ratio of DMB:AMA=4:1

From the obtained data of the catalytic process of [4+2]-cyclic addition of DMB and AMA (Fig. 11), the optimum catalyst $Ag_{n.p.}$, was chosen since its use provides the maximum (76 %) ATMCHC yield.

According to the decrease in the catalytic activity in reactions of [4+2]-cyclic addition of DMB and esters of acrylic acids, the catalysts stand in this order: $Ag_{n.p.} > Cu_2Cl_2 > Pd_{n.p.} > Au_{n.p.}$.

The conducted studies of the effect of temperature, molar ratio of reagents, nature of catalysts and analysis of the obtained results allowed us to establish optimal conditions for the processes of obtaining ATMCHC. It was established that for the reaction of the catalytic [4+2]-cyclic addition of DMB and AMA, the optimum conditions are as follows: the temperature interval 323–333 K and the molar ratio DMB:AMA=4:1. The ATMCHC yield in this case reaches 71 to 76 % with the productivity of the process of 116 g/l·h.

The catalytic synthesis of esters of alkylcyclohexenecarbonic acids was carried out at a temperature of 333 K and a molar ratio of reagents DMB:acrylic acid ester=4:1 and addition of $Ag_{n.p.}$ in an amount of 0.25 % mol of the weight of ester of alkylacrylic acid. The starting mixture of reagents and catalyst was loaded into a 30 cm^3 reactor with a magnetic stirrer and connected to a thermostat and a refrigerator. After 5 hours, the reaction mixture was cooled and analyzed by chromatography.

The reaction mixture was separated in two steps: initially, by distillation of the reaction mixture at atmospheric pressure in a flask equipped with a dephlegmator of 20 cm in length until reaching a maximum still temperature of 345 K and separation of the residual DMB. Then, acrylic acid ester was separated while raising temperature to 380 K. After this, the distillation process was carried out in vacuo (2 gPa), and ester of alkylcyclohexenecarbonic acid was separated at 375 K and a small amount of azeotrope was left in the still.

On the basis of the balance syntheses, material balance of the catalytic process of obtaining ATMCHC was made (Table 4).

Table 4

The material balance of the process of obtaining ATMCHC under optimal conditions: temperature: 333 K, molar ratio: DMB:AMA=4:1, catalyst: $Ag_{n.p.}$ (0.25 % mol), Q=117 g/l·year

Loaded	g	mol	Obtained	g	mol	Yield, %
1. DMB	164.00	2.00	1. ATMCHC	79.04	0.38	76.00
			2. DMB (nonreacted)	132.82	1.62	–
2. AMA	63.00	0.50	3. AMA (nonreacted)	14.76	0.12	
			4. Azeotrope (losses)	0.40	–	
3. $Ag_{n.p.}$	7.87	–	5. $Ag_{n.p.}$	7.87	–	
Total	234.87	–	Total	234.87	–	

The synthesized allyl-1,3,4-trimethylcyclohex-3-enecarboxylate has the following physical and chemical characteristics: T_{boil}=375/4 K/gPa, $n_D^{293} = 1.4758$, MR=61.31 (found), 61.09 (calc.)

NMR 1H spectrum of ATMCHC. The NMR 1N spectrum is completely consistent with the ATMCHC structure. The spectrum has signals at 1.38, 1.82, 1.82, 1.84, 1.91, 2.01, 2.09, 2.15, 2.40, 4.75, 5.23, 5.24, 6.06 ppm. The protons of the allyl fragment are recorded at 6.06 ppm. in a form of a multiplet, at 5.23, 5.24 ppm. in a form of a triplet and at 4.75 ppm in a form of a doublet. Six protons of the cyclohexene fragment give four doublet signals at 1.84, 1.91, 2.01, 2.09, 2.15, 2.40 ppm. The methyl groups in the cycle in 1, 3, 4 positions resonate as two singlets at 1.38, 1.82, 1.82 ppm.

Esters of alkylcyclohexenecarbonic acids can be used as monomers for manufacture of hyper plasticizers. Output of experimental batches of esters of alkylcyclohexenecarbonic acids was realized in accordance with the developed technical specifications TU U 24.1-02071010-159:2013 at the pilot plant of Galichina Scientific and Production Co.

Previous studies were conducted with the use of a new monomer of ATMCHC for synthesis of concrete hyper plasticizers [25]. These samples of hyper plasticizers obtained by copolymerization of ATMCHC with methacrylic acid and monocaprylate of polypropylene glycol have shown positive results in concrete mixtures (Table 5).

Table 5

Influence of addition of hyper plasticizer on concrete mixtures

Indicator	Cone settling, cm	Cone spread, cm	Setting time, days	Freezing resistance, F	Impermeability to water, W	Freezing point, K	Movableness, hrs
With no hyper plasticizer	18–20	50	30	100	7–9	268	1–2
With hyper plasticizer	>25	>60	15	500	>16	253	3–6

The use of hyper plasticizers enables cone settlement more than 25 cm and cone spread over 60 cm which greatly accelerates the process of concrete solidification, increases frost resistance and, consequently, up to 5 times higher durability of concrete (from F100 to F500). Adding of the hyper plasticizer increases impermeability to water by several degrees, up to W 16 and higher. Accordingly, it is not necessary to apply special waterproofing measures for the final product. Hyper plasticizer in concrete mixtures has the ability to reduce freezing point of concrete to 253 K which ensures work at any time of the year. Concrete with addition of hyper plasticizer has the effect of preserving mobility of the concrete mixture from 3 to 6 hours without reducing the cone settling, thereby allowing transportation of concrete over long distances without degradation of its quality. Addition of hyper plasticizer makes it possible to obtain a glossy surface in manufacture of decorative concretes.

Such concrete mixtures possess hyperplastifying properties and enable preparation of a self-compacting concrete that does not require vibration. This is due to force out air pores which is important in monolithic concrete construction, manufacture of prefabricated elements with a highly developed reinforcement system by the cassette method.

The essence of this production process consists in the use of a hyper plasticizer liquid enabling change of physical and mechanical properties of concrete mixtures due to the plasticizing effect. In this case, parameters are obtained with specific requirements of durability, mobility, useful life as well as frost resistance, water impermeability and other important characteristics. The advantage of adding hyper plasticizers in concrete mixtures is not only to improve their parameters but also reduce the cost of final products as the need for additional processing of concrete mixtures disappears.

Polymer compositions created with participation of ATMCHC are recommended for making contact lenses and artificial crystalline lenses as they free eyes from the feeling of dryness, redness and edema of the cornea. Due to sufficient moisture content (50–60 %), they provide comfortable wear and allow people to wear each pair of lenses for a month without removing them. An important indicator for contact lenses is air permeability. Because of its unique structure, the iris has no blood vessels and its cells receive oxygen from atmospheric air. The lens inevitably complicates this process and in a case of lack of air permeability, it can cause hypoxia of the iris and germination of blood vessels in it. In this way, organism compensates oxygen starvation of the cells. The bottom threshold of air permeability established in the course of numerous ophthalmological studies is 125 units. These polymeric materials can provide this indicator at a level of 150 units.

No less important is the radius of curvature. To make the eyes comfortable and prevent the contact lens from "swimming off" caused by blinking, its inner radius should correspond to the size of the eyeball. If the lens is large, it is badly fixed on the iris and can easily fall out and if the radius is less than necessary, the lens will compress the cornea that results in dryness and discomfort of its wearing. The radius of curvature must be within the range 8.2–8.9 BC. The radius of curvature of the manufactured contact lenses from the polymeric materials based on ATMCHC was found to be 8.4 BC.

Taking into account all of these indicators, the ATMCHC based polymeric materials are recommended for the manufacture of contact lenses.

Since the crystalline lens is one of the main optical elements of the eye which focuses the image of objects on the retina, its removal because of cataract requires mandatory optical correction. The artificial crystalline lens consists of an intraocular lens and supporting elements completely covered with a carbon diamond-like envelope and is intended for internal eye prosthetics in the reconstructive surgery. Its main technical characteristics are thickness of the film on the intraocular lens which should not exceed the degree of roughness according to the class of purity. Thickness of the film on the supporting elements should be within 1°5 microns. The use of ATMCHC based polymeric compositions for making the intraocular lenses can provide satisfactory technical characteristics of artificial crystalline lenses and therefore can be used in the process of their manufacture.

6. Discussion of the results obtained in the study of the reaction of catalytic cyclic addition of 2,3dimethylbuta-1,3-diene and allyl methacrylate by the Diels-Alder reaction

It was established that in the presence of $Ag_{n.p.}$ catalyst, reaction of [4+2]-cyclic addition of DMB and esters of acrylic acids proceeds according to a two-stage mechanism through the initial stage of formation of a catalytic complex which activates the reaction by reducing its energy barrier by 44 kJ/mol.

Optimal conditions of the catalytic process are determined on the basis of kinetic regularities and studies on the influence of temperature, molar ratio and nature of the catalyst: temperature of 323–333 K and the molar ratio of reagents DMB:AMA=4:1 in the presence of $Ag_{n.p.}$ catalyst (0.25 % mol), the maximum yield of ATMCHC is 72–76 % at a productivity of 111-117 g/(l/hr).

The esters of alkylcyclohexenecarbonic acids synthesized in this work can be subjected to polymeric transformations and used as a raw material for preparation of polymeric materials, compositions and hyper plasticizers of concrete mixtures [25]. The polymer compositions obtained with participation of ATMCHC are recommended for manufacturing contact lenses and artificial intraocular lenses.

These studies are a continuation of earlier studies of the non-catalytic reaction to obtain esters of alkylcyclohexenecarbonic acids [26]. The yield of target products in application of the catalytic method makes up 72–76 %. Such a yield is due to steric difficulties of ATMCHC which hinder further interaction of the catalytic complex and the starting reagents. A high yield on an industrial scale will create the advantage of lowering the reaction energy barrier. Given the significant reduction in temperature for the catalytic process, this will reduce energy costs of production and will ensure a positive economic effect. There are no limitations on the use of this study data in production since its hardware introduction does not require significant changes and modernization.

Availability of a homologous series of alkylmethacrylates and a variety of catalysts creates a practical opportunity for continuation of studies in this area. In further improvement of this catalytic study, it is necessary to take into account the structural features of the final products. In the course of the study, it may be difficult to find practical use of new substances since it is not known in advance what properties they will possess.

7. Conclusions

1. Optimal conditions of the catalytic process such as temperature of 323–333 K and the molar ratio of reagents DMB:AMA=4:1 in the presence of a $Ag_{n.p.}$ catalyst (0.25 % mol), maximum ATMCHC yield of 72–76 % at a productivity of 111–117 g/(l/hr) were established.

2. Based on the obtained kinetic and activation parameters, it has been proved that the catalytic reaction of obtaining ATMCHC is subject to the kinetic law of the second order and is energy-efficient, E_{akt}=32.6 kJ/mol.

3. The synthesized esters of alkylcyclohexenecarbonic acids are recommended as a raw material for production of polymeric materials for contact lenses, artificial crystalline lenses and hyper plasticizers of concrete mixtures.

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