

The use of a modern homogeneous metal complex catalyst for the hydration of acetylenes is being investigated. The process is relevant both for the industry of basic organic synthesis and for the perfume industry. The analysis of existing processes used in industry for the production of acetaldehyde was carried out. Significant shortcomings of existing processes are revealed: low environmental friendliness and high energy consumption. To solve this problem, the reaction of hydration of an acetylene compound was studied using a modern homogeneous catalyst based on gold, which is not toxic. The study was conducted by selecting aliquots during the reaction. Using the ^1H NMR spectroscopy method, the conversion values of phenylacetylene were calculated for the time values corresponding to the moments of aliquot sampling. The reaction order with respect to phenylacetylene was calculated and the reaction constant under the reaction conditions was calculated. When reacting in the presence of the proposed catalyst, a conversion of phenylacetylene of 86.96 % is achieved in 3 hours. The data obtained provide grounds for carrying out the process of catalytic hydration of acetylenes, namely phenylacetylene, with the production of acetophenone, which is important for use in the perfume industry. The data obtained can be applied to the process of hydration of acetylene with the formation of acetaldehyde, which is widely used in the industry of basic organic synthesis. For the process of catalytic hydration of acetylene compounds, a hardware design is proposed, a gas-liquid reactor with a changing hydrodynamic situation, which, together with the product separation column, is combined into a single installation. Using an optimized method, a catalyst based on gold chloride was synthesized from a gold alloy

Keywords: homogeneous metal complex catalysis, gold, triphenylphosphine, hydration, acetylene, acetaldehyde, phenylacetylene, acetophenone

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PREPARATION OF AURUM CHLORIDE COMPLEX AND ITS USE FOR INDUSTRIAL ACETYLENE HYDRATION CATALYST PROCESS

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1. Introduction

The industry of basic organic synthesis constantly retains its relevance and is in the process of constantly searching for new and improving existing processes. The products of the main organic synthesis, the so-called organic commodity chemicals, are actively used as reagents for the large-scale production of various commercial products, such as dyes, pesticides, cosmetics and detergents. One of the modern and relevant areas where products of basic organic synthesis are actively used is the production of monomers for plastics, synthetic fibers and synthetic rubber. In modern conditions, the use of polymeric materials is constantly expanding, which leads to a further increase in the production of monomers. Therefore, one of the products of the main organic synthesis, the production of which is constantly growing, is acetaldehyde, which is used as an intermediate product in the production of various monomers. Acetaldehyde is a volatile liquid with a boiling point of 20.8 °C, readily soluble

in water, and in the presence of acids forms a liquid cyclic trimer, paraldehyde, which can later be recycled back into acetaldehyde [1]. Acetaldehyde is an intermediate product of the basic organic synthesis industry and is used to produce acetic acid, acetic anhydride, n-butanol, pentaerythritol, and other valuable products [2]. With this wide application, the acetaldehyde market was valued at 1.33 billion USD in 2017 and is projected to reach 1.80 billion USD in 2022 at a CAGR of 6.24 % over the forecast period [3]. Therefore, scientific research that contributes to the development of new or significant improvement of existing industrial processes for the production of acetaldehyde is important, and the results of such research are needed in practice, as they allow building environmentally friendly and energy-saving processes. An important way to improve existing industrial catalytic processes is the creation and industrial application of new or already existing homogeneous metal complex catalysts. Such catalysts make it possible to efficiently carry out processes at low temperatures and atmospheric pressure.

The use of homogeneous metal complex catalysts makes it possible to significantly modernize the industrial process of catalytic hydration of acetylene compounds. With the help of the catalytic hydration process, acetophenone can also be obtained, which, like some of its derivatives, is used in the perfume industry. In particular, acetophenone derivatives such as 2-aminoacetophenone, linalool, E-(8)-oxolinalool and lilac aldehyde, which are aromatic substances that convey the smell of bird cherry and other similar floral odors. To obtain acetophenone, the process of catalytic hydration of phenylacetylene is used.

2. Literature review and problem statement

One of the main ways to obtain acetaldehyde is the catalytic hydration of acetylene, which is described in [4] Wacker process. Acetylene in the modern industry of basic organic and petrochemical synthesis is preferably obtained by high-temperature pyrolysis of methane and other hydrocarbons, as noted in [1]. It should also be noted that in modern social conditions, a decrease in the production of motor fuels for road transport is predicted. This trend is associated with the active use of electric vehicles and hybrid engines by many automakers. Accordingly, the depth of oil refining at the enterprises of the industry will probably increase, which will increase the availability of hydrocarbons for use in basic organic synthesis. These predicted trends will thus increase the demand for new technologies for the efficient processing of petrochemicals and, in particular, acetylene.

Given the above, the object of research and further improvement is the process of catalytic hydration of acetylene. Historically, the main industrial method for obtaining acetaldehyde from acetylene is a process based on the Kucherov reaction. The paper [5] describes the process of catalytic hydration of acetylene. This process is based on the addition of water to acetylene in the presence of a catalyst – a solution of mercury (II) sulfate HgSO_4 in sulfate acid. To understand the shortcomings of this process and ways to develop new, more environmentally friendly and energy-saving processes, it is necessary to dwell on this process in more detail. The catalyst in the Kucherov reaction is mercury sulfate (II). But the issues related to the introduction of this process into the industry remained unresolved. Due to a subsequent request for increased production of acetaldehyde, the process was formalized for industrial use. Such an application of the process based on the Kucherov reaction is described in [6]. The process is implemented as follows. The reactor, also called the acetaldehyde generator, is preliminarily filled with contact acid, which is a solution of iron (III) sulfate $\text{Fe}_2(\text{SO}_4)_3$ in sulfate acid. During the reaction, intermediate compounds are formed from salts of mercury and acetylene, which further add water to acetylene, resulting in the formation of acetaldehyde. It should be noted that during the process, the contact acid loses its activity due to the gradual accumulation of iron (II) sulfate FeSO_4 in it. Therefore, in the process based on the Kucherov reaction, there is a need for constant removal of the used contact acid from the reactor for regeneration. Regeneration is a process of treating the withdrawn contact acid with 25 % HNO_3 nitrate acid, which is a strong oxidizing agent. Also, as part of the technological process, they mean the addition of metallic mercury to the reactor, which is associated with the loss of part of the

mercury during the regeneration of the contact acid. The process temperature is 97 °C, atmospheric pressure, the yield is about 90 % of theoretical for acetylene.

Despite the fact that the process based on the Kucherov reaction has a fairly high level of conversion, a number of issues remain unresolved. Chief among them is the high toxicity of the Hg^{2+} salts used, which prevents the wide application of this process, as indicated in [7]. But due to the low level of application of homogeneous metal complex catalysis at that time, the issue was not resolved. The second problematic issue is that in order to carry out the process based on the Kucherov reaction, it is necessary to sparge acetylene with high intensity through the contact acid layer. This requires the use of high power compressors and, as a result, leads to high energy costs. Given the requirements of the current application of the principles of Green Chemistry in the chemical industry, this process needs to be replaced by a more environmentally friendly and energy efficient one.

Considering the importance of acetaldehyde as an intermediate product in the industry of basic organic synthesis, the search for new ways to obtain it did not stop. It should be noted the development of the 60 s of the last century, in which the production of acetaldehyde occurs by direct oxidation of ethylene, based on the Wacker process. Specified process currently used in the industry can be either single-stage or two-stage. The one-step process assumes that ethylene and oxygen streams meet simultaneously in a reaction tower at a temperature of about 130 °C and a pressure of 400 kPa, using a catalyst that is an aqueous solution of PdCl_2 and CuCl_2 . The description of this process is given in [2]. It is shown that in a two-stage process, the oxidation reaction is carried out separately in tubular reactors. In contrast to the one-stage process, air can be used instead of oxygen in the two-stage process, which is also described in [2]. Ethylene is passed through the reactor together with the catalyst at a temperature of 105–110 °C and a pressure of 900–1,000 kPa. The catalyst is separated from the reaction mass by distillation. The catalyst is then oxidized in a reactor at 1,000 kPa using air as the oxidizing medium. The oxidized catalyst solution is separated and recycled to the reactor.

Both one- and two-stage processes are used in industry, designed to produce acetaldehyde by direct oxidation of ethylene and based on the Wacker process. For both processes, issues related to the need to use high pressures and temperatures remain unresolved, so they are quite complex in terms of instrumentation. In addition, rather expensive palladium catalysts are used in these processes. An option to overcome the corresponding difficulties may be the development of new homogeneous catalysts, in which the complexing agent will be a less expensive metal.

Therefore, the issue of developing a new process for the production of acetaldehyde is quite relevant. At the same time, the main areas of improvement are, on the one hand, environmental friendliness (as opposed to the Kucherov process). On the other hand, it is desirable that the new process can be carried out at atmospheric pressure and low temperature (unlike the Wacker process). It is also desirable to use relatively inexpensive and recoverable catalysts in the new process.

It is important to additionally note that the industrial use of acetaldehyde was initially mainly concentrated on its use as a starting material in processes related to the production of acetic acid. Competing processes also used to produce

acetic acid in industry are two processes. Historically, the Monsanto process was developed first, followed by the Cativa process. In both of these processes, acetic acid is produced not from acetaldehyde, but from methanol. However, both of these processes have a number of significant drawbacks. Thus, both processes are carried out at high pressures in the range from 3 to 6 MPa and at a temperature in the range from 150 to 200 °C. In addition, quite complex and expensive catalysts are used in both processes, in the Monsanto process these are rhodium complexes, namely the $\text{cis-}[\text{Rh}(\text{CO})_2\text{I}_2]^-$ anion and in the Cativa process, it is $[\text{Ir}(\text{CO})_2\text{I}_2]^-$.

The application of the process of catalytic hydration of acetylene compounds is not limited to the hydration of acetylene. Also, this process can be successfully applied in other industrial productions with a smaller tonnage, but at the same time no less in demand in the modern economy. In particular, a possible direction of using the studied catalytic process is its application for the production of such an important intermediate as acetophenone. It was shown in [8] that acetophenone, together with a number of its derivatives, is widely used in the perfume industry. This is possible because its derivatives can convey the smell of bird cherry and other similar floral odors, as indicated in [9]. Among compounds similar in structure to acetophenone and interesting for use as fragrant substances, it is possible to note 2-aminoacetophenone, linalool, E-(8)-oxolinalool, and lilac aldehyde. In the case of the application of the process under study in the perfume industry, it should be noted that phenylacetylene is a necessary precursor for the production of acetophenone. This allows to state that it is advisable to conduct a study on the development of a process for the production of acetophenone. In turn, the production of phenylacetylene can be built on the basis of the process described in [10], which presents the results of studies on the production of acetophenone from β -bromostyrene by the action of molten potassium hydroxide. It is this approach that was used in [10], where β -bromostyrene is used as a precursor, which may be of interest specifically for the perfume industry, since β -bromostyrene itself is a substance used as a fragrant substance and is used as a fragrance. soap, as indicated in [11].

Considering the possibilities of industrial application of the process under study and, in particular, that obtained by the catalytic hydration of acetophenone, it is impossible to ignore its possible use in the field of polymers. Thus, in [12], the results of studies are presented and it is noted that commercially important resins can be obtained by treating acetophenone with formaldehyde and alkali. The copolymers thus obtained are conditionally described by the formula $[(\text{C}_6\text{H}_5\text{COCH})_x(\text{CH}_2)_x]_n$ and are the result of aldol condensation. These substances are components of coatings and paints. Modified acetophenone-formaldehyde resins are obtained by hydrogenation of the above-mentioned resins containing ketones. As shown in [13], the resulting polyol can be additionally cross-linked with diisocyanates, and therefore these modified acetophenone-formaldehyde resins are contained in coatings, paints, and adhesives.

Therefore, the development of new processes for the production of acetaldehyde using lower pressures and temperatures and using less expensive metals as complexing agents is topical. The development of new processes for the production of acetaldehyde will significantly increase the share of its use as a starting material in processes associated with the production of acetic acid.

As one of the possible directions for the creation of such new processes, there is a significant improvement in the process of catalytic hydration of acetylene considered above, but with the use of modern homogeneous metal complex catalysis. Choosing a new catalyst to improve the process of catalytic hydration of acetylene, the goal was to obtain not only a high level of conversion of phenylacetylene, but also moving in parallel with modern trends, to create an energy efficient and environmentally friendly process.

Taking into account these requirements, as well as the fact that catalysis based on gold is rapidly developing in the 21st century, which is indicated in [14, 15], this suggests that it is expedient to conduct a study on the use of catalysts based on gold with ligands of the triphenylphosphine type in the process of catalytic hydration of acetylene, as indicated in [16, 17]. Considering all of the above, the problem of finding a catalyst for the hydration reaction that will work at atmospheric pressure and will not be toxic, but at the same time be hydrophilic and reproducible, is an urgent problem. To solve this problem, a gold chloride catalyst with triphenylphosphine trisulfonic acid sodium salt (TPPTS) as a ligand and a chlorine atom as a counterion, $[\text{AuCl}(\text{TPPTS})]$ was used. The use of this catalyst makes it possible to carry out the process of catalytic hydration of acetylenic compounds at sufficiently low temperatures and atmospheric pressure, achieving high levels of phenylacetylene conversion. An important advantage of the considered catalyst is the environmental safety of its use. But there are still unresolved issues related to both the optimal method for obtaining the catalyst and the development of industrial processes using the $[\text{AuCl}(\text{TPPTS})]$ catalyst. The reasons for this may be in the absence of kinetic studies in relation to such processes. A variant of overcoming the corresponding difficulties may be to conduct kinetic studies according to a detailed method. All this allows to state that it is expedient to conduct a study on the kinetics of the hydration of acetylenes using the $[\text{AuCl}(\text{TPPTS})]$ catalyst.

3. The aim and objectives of the study

The aim of the study is to develop an improved and modern process for the catalytic hydration of acetylenic compounds using a homogeneous gold-based metal complex catalyst with triphenylphosphine-type ligands. This will make it possible to obtain a new industrial process for the catalytic hydration of acetylenes, which will meet modern requirements for environmental friendliness and energy saving.

To achieve the aim, the following objectives were set:

- to obtain a catalyst $[\text{AuCl}(\text{TPPTS})]$ based on gold, with triphenylphosphine trisulfonic acid sodium salt as a ligand and a chlorine atom as a counterion;
- to develop a methodology and conduct a kinetic experiment on the hydration of acetylene compounds using the example of phenylacetylene;
- to determine the rate constant of the reaction of hydration of acetylenic compounds using the example of phenylacetylene on the catalyst $[\text{AuCl}(\text{TPPTS})]$;
- to develop a technological scheme for the process of catalytic hydration of acetylene on the catalyst $[\text{AuCl}(\text{TPPTS})]$.

4. Materials and methods of research

The object of research is the process of catalytic hydration of acetylenic compounds using a homogeneous metal complex catalyst based on gold with ligands of the triphenylphosphine type. The main hypothesis of the study is the possibility of carrying out the process of catalytic hydration of acetylenes with a high level of conversion, at low temperatures and atmospheric pressure. The simplifications adopted in the study refer to the fact that in order to study the process of hydration of acetylenes with the $[\text{AuCl}(\text{TPPTS})]$ catalyst, the process was carried out with phenylacetylene. This compound is an analogue of acetylene, but is more convenient and safe due to the liquid state of aggregation, in contrast to gaseous acetylene.

The following reagents were used in the study:

1. Gold, chemically pure.
2. Chloric acid, 36.5 %, chemically pure.
3. Nitrate acid, 70 %, chemically pure.
4. Sulfuric acid, 96 %, chemically pure.
5. Sodium borohydride, chemically pure.
6. Dimethyl sulfoxide, chemically pure.
7. Triphenylphosphine trisulfonic acid sodium salt, chemically pure.
8. Methanol, chemically pure.
9. Ethanol, chemically pure.
10. Isopropanol, chemically pure.

The $[\text{AuCl}(\text{TPPTS})]$ complex was obtained using a laboratory unit shown in Fig. 1.

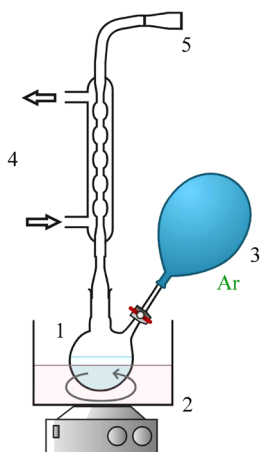


Fig. 1. Laboratory unit for obtaining the $[\text{AuCl}(\text{TPPTS})]$ complex (the scheme was created using the Chemix online service): 1 – reaction mixture containing the complex $[\text{AuCl} \cdot (\text{CH}_3)_2\text{S}]$, TPPTS prepared according to the procedure, and a mixture of water with acetonitrile; 2 – heated stirrer and oil bath; 3 – reservoir with argon; 4 – cooling; 5 – calcium chloride tube; Ar is argon

To carry out the kinetic experiment of phenylacetylene hydration, let's use the laboratory unit shown in Fig. 2.

Processing of selected aliquots was carried out using the laboratory unit shown in Fig. 3.

All ^1H NMR spectra were obtained on a Varian Union Plus device (400 MHz), chemical shifts were determined from residual solvent signals. The content of carbon and hydrogen was determined by the Pregl gravimetric method.

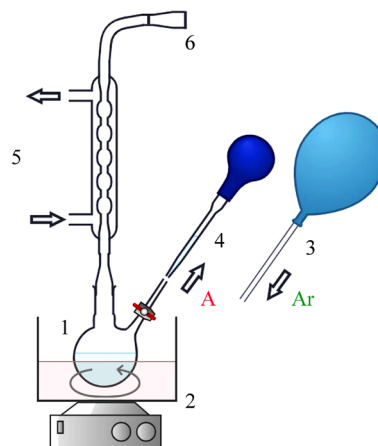


Fig. 2. Laboratory unit for conducting a kinetic experiment of phenylacetylene hydration (the scheme was created using the Chemix online service): 1 – reaction mixture containing distilled phenylacetylene dissolved in methanol and water with the addition of a small amount of cocatalyst; 98 % sulfuric acid; 2 – heated stirrer and oil bath; 3 – reservoir with argon; 4 – pipette for taking aliquots; 5 – cooling; 6 – calcium chloride tube; A – aliquot; Ar – argon

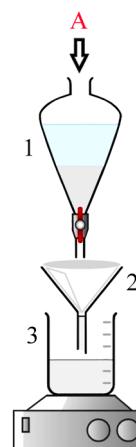


Fig. 3. Laboratory unit for processing selected aliquots (the scheme was created using the Chemix online service): 1 – separation and drying of the organic layer of the mixture, which includes an aliquot together with water and dichloromethane added according to the method; 2 – filtration of the organic layer; 3 – evaporation; A – aliquot

5. Results of the study of the acetylenes hydration process using the complex of gold chloride as a catalyst

5.1. Preparation of $[\text{AuCl}(\text{TPPTS})]$ catalyst based on gold with triphenylphosphine ligands

To obtain catalyst 7, gold in the form of alloy 3 was dissolved in a mixture of concentrated chloride and nitrate acids. As a result, HAuCl_4 4 was obtained, which was reduced with NaBH_4 and dispersed gold 5 was obtained. Dispersed gold 5 was boiled in a mixture of dimethyl sulfoxide with concentrated hydrochloric acid. After cooling, gold complex with dimethyl sulfide 6 precipitated. As a result of mixing complex 6 with TPPTS, target catalyst 7 was obtained. The general conversion scheme is shown in Fig. 4.

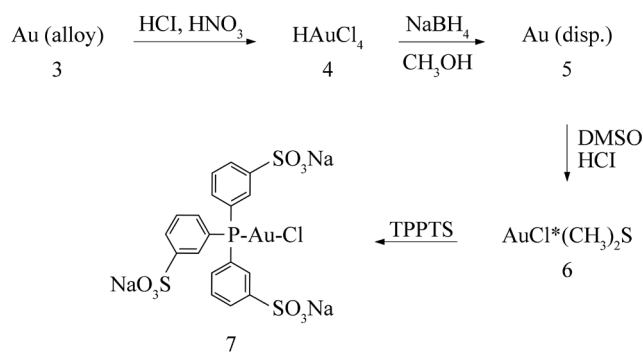


Fig. 4. Scheme for the synthesis of [AuCl(TPPTS)]

Preparation of dispersed Au(5).

In a 50 ml round bottom flask with a magnetic Teflon anchor and a reflux condenser, to 1 g (5.08 mmol) of finely chopped Au were added 5.2 ml (61.36 mmol) of 36.5 % aqueous HCl and 1.2 ml (11.45 mmol) 60 % aqueous HNO₃. The reaction mixture was heated until a homogeneous orange reaction mixture was formed. After cooling, the reaction mixture was evaporated on a rotor. After evaporation, 1 ml of 36.5 % aqueous HCl was added and evaporated again. This procedure was repeated 3 times. The resulting HAuCl₄·nH₂O precipitate was lyophilized and dissolved in 20 ml of methanol in a 50 ml round bottom flask with a Teflon anchor. 0.5 g (13.22 mmol) of NaBH₄ was added in portions to the solution, and the evolution of hydrogen and the formation of a dispersed precipitate were observed. The precipitate was filtered on a S4 glass filter and washed with water and dried. A precipitate weighing 0.64 g was obtained. Yield 64 %.

Preparation of [AuCl(CH₃)₂S](6) complex.

0.64 g of dispersed Au was placed in a 50 ml round bottom flask with a magnetic Teflon anchor and a reflux condenser. To the flask were added 8 ml (112.63 mmol) of dimethyl sulfoxide and 16 ml (188.8 mmol) of 36.5 % aqueous HCl. The reaction mixture was boiled for 2 hours in an oil bath. After cooling, a white precipitate formed, which was filtered on a S3 glass filter and washed with a 1:1 hexane/ethanol mixture. The resulting precipitate was dried to give 0.7 g. Yield 73 %. ¹H NMR (CDCl₃): 2.69 (c, 6H, S(CH₃)₂). Calculated for C₂H₆AuClS: C 8.16, H 2.05. Found: C 8.14, H 2.04.

Preparation of [AuCl(TPPTS)] complex (7).

In a 500 ml round bottom flask in a magnetic Teflon anchor and under argon atmosphere, 0.7 g (2.38 mmol) of complex 6 of 1.4 g (2.47 mmol) TPPTS was mixed in 200 ml of a mixture of water with acetonitrile in a ratio of 1:1. The reaction mixture was stirred for 1.5 h at 25 °C. The reaction mixture was evaporated and the resulting precipitate was taken up in dichloromethane and filtered off. The filtrate was dried to give 1.5 g of a white crystalline solid. Yield 76 %. ¹H NMR (dmsO-d₆): 7.37–7.42 (m, 3H, CH), 7.56–7.60 (m, 3H, CH), 7.82–7.86 (m, 6H, CH). Calculated for C₁₈H₁₂AuClNa₃O₉PS₃: C 27.00, H 1.51. Found: C 27.04, H 1.53.

5.2. Conducting a kinetic experiment of phenylacetylene hydration

The [AuCl(TPPTS)] catalyst was tested on phenylacetylene 1, which is an analogue of acetylene and is more convenient due to the liquid state of aggregation, in contrast to gaseous acetylene. Fig. 5 shows a diagram of the phenylacetylene hydration.

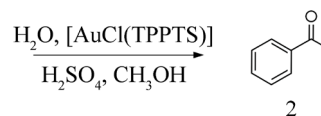


Fig. 5. Hydration scheme of phenylacetylene with [AuCl(TPPTS)]

The following methodology was developed for conducting a kinetic experiment on the hydration of acetylene compounds using phenylacetylene as an example. A 500 ml reactor with a magnetic Teflon anchor and reflux condenser was used. Phenylacetylene 2 g (19.58 mmol) was added to the reactor under argon atmosphere. Phenylacetylene was dissolved in 200 ml of methanol and 40 ml of water. To the solution were added 0.32 g (0.40 mmol) of catalyst 7 and 0.02 ml (0.40 mmol) of 98 % sulfuric acid. The temperature was brought to 65 °C and aliquots were taken. Aliquots were taken every 10 minutes for 90 minutes. Another 2 aliquots were taken at 120 and 180 minutes after the start of counting. For aliquots, 5 ml of the reaction mixture was taken and added to 20 ml of water and 20 ml of dichloromethane. The organic layer was separated and dried with Na₂SO₄, filtered and evaporated. The resulting mixture was sampled on ¹H NMR spectrum in CDCl₃ to set the conversion of phenylacetylene.

5.3. Determination of the hydration reaction constant of acetylenic compounds using the example of phenylacetylene on the catalyst [AuCl(TPPTS)]

To determine the rate constant of the reaction of hydration of phenylacetylene with [AuCl(TPPTS)], an experiment was carried out in which aliquots were removed during the reaction to obtain the conversion of phenylacetylene. The reaction was carried out in methanol/water in a ratio of 5:1 at 65 °C. Sulfuric acid acted as a cocatalyst. The conversion versus reaction time is shown in Table 1, with the 50 min point being an outlier and therefore not shown in the table. The catalyst and co-catalyst were taken in the amount of 0.02 eq.

Table 1

Time dependence of phenylacetylene conversion in the hydration reaction

Time, min	Conversion, %
10	23.7
20	31.6
30	50.0
40	59.5
60	68.0
70	69.0
80	70.4
90	71.4
120	80.0
180	87.0

The phenylacetylene conversion degree was determined by integrating the signals of the acetylenic and acetyl groups in ¹H NMR spectra. The acetylene group is at 3.10 ppm and the acetyl group is at 2.63 ppm. The acetylene group corresponds to an example of a fragment of the ¹H NMR spectrum at 23.70 % conversion, shown in Fig. 6.

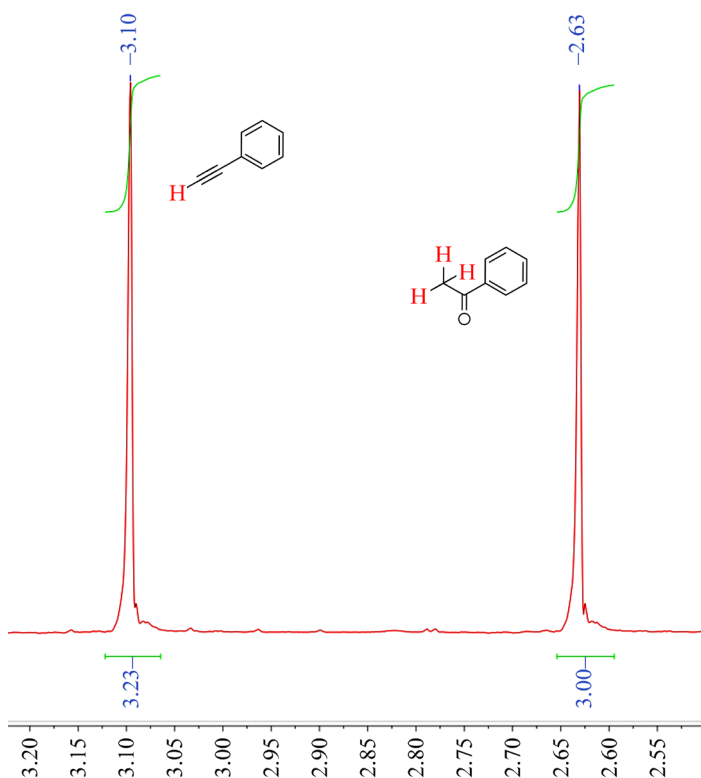


Fig. 6. ¹H NMR spectrum of the reaction of phenylacetylene hydration at 10 min

The next step was to determine the order of the reaction. Given the fact that water acts as a reagent and as a solvent, it is taken in large excess and does not affect the order of the reaction. The order of the reaction was considered only for phenylacetylene. To calculate the order of the reaction, the Van't Hoff methods were used and for parameters $\tau_{1/2}$ and $\tau_{1/4}$.

Van't Hoff method. To calculate the order of the reaction by this method, let's obtain the reaction rates V at certain points $\frac{dC}{dt}$ and plotted the dependence graph $\ln V=f(\ln C)$, which is shown in Fig. 7. This dependence was linearized by the least squares method and the order of the reaction was equal to 1.75 ± 0.51 .

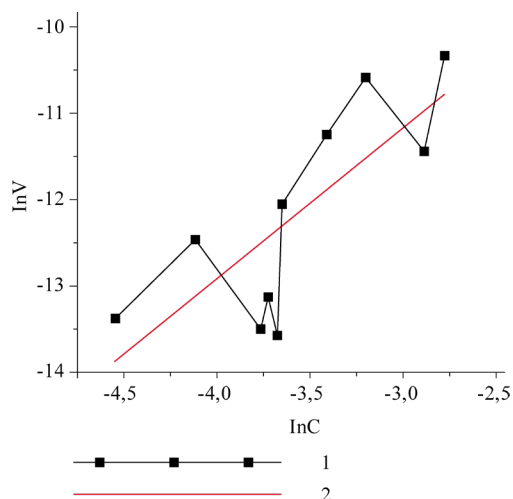


Fig. 7. Dependence graph $\ln V=f(\ln C)$:
1 – dependence graph; 2 – least squares linearization

Method by parameters $\tau_{1/2}$ and $\tau_{1/4}$. To calculate the reaction order by this method, let's use (1)

$$n = \frac{\ln\left(\frac{t_2 - t_1}{t_1}\right)}{\ln\frac{C_0}{C_0/2}} + 1 = \frac{\ln\left(\frac{t_2 - t_1}{t_1}\right)}{\ln 2} + 1, \quad (1)$$

where t_1 – the time at which half of the concentration of the starting substance remains in the reaction mixture, t_2 – the time at which a quarter of the concentration of the starting substance remains in the reaction mixture. To calculate these parameters, a dependence graph $C=f(t)$ was plotted, which is shown in Fig. 8.

The initial concentration of phenylacetylene in the reaction was 0.082 mol/l, hence the half concentration is 0.041 mol/l and the quarter concentration is 0.0205 mol/l. These concentrations correspond to the values of t_1 and t_2 , equal to 1800 s and 6200 s, respectively, Fig. 8. Substituting t_1 and t_2 into (1), let's obtain the value 2, equal to the reaction order according to this method.

Based on the two methods described above, it can be said that the order of the phenylacetylene hydration reaction under the conditions described in the experimental part is 2.

For 2nd order reactions, the kinetic equation is calculated according to (2)

$$-\frac{dC}{dt} = kC^2. \quad (2)$$

Accordingly, its integration (3)

$$\frac{1}{C} = \frac{1}{C_0} + kt. \quad (3)$$

To obtain the reaction constant, let's plot the dependence $1/C=f(t)$, shown in Fig. 9.

After carrying out the linearization using the least squares method, the dependences $1/C=f(t)$ obtained the reaction rate constant equal to $7.3 \pm 0.3 \cdot 10^{-3} \text{ l}/(\text{mol} \cdot \text{s})$.

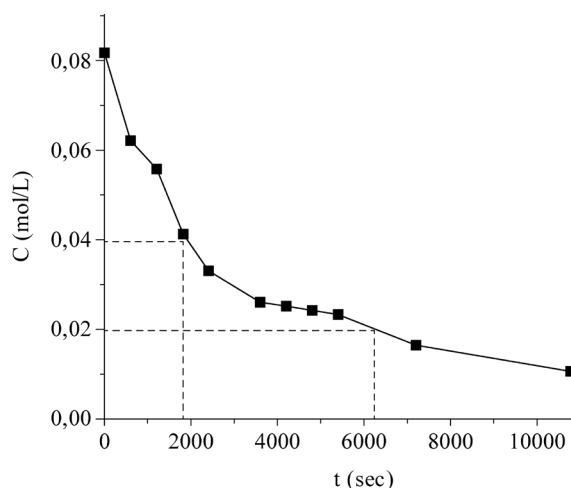


Fig. 8. Dependence graph $C=f(t)$

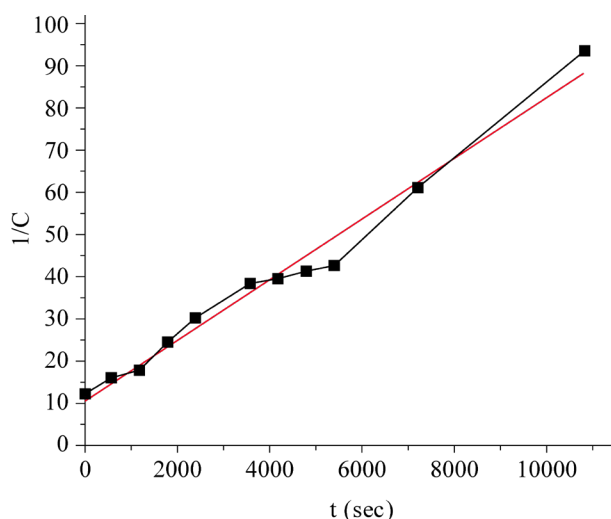


Fig. 9. Dependence graph $1/C=f(t)$: 1 – dependence graph; 2 – least squares linearization

5.4. Development of a technological scheme for the process of catalytic hydration of acetylene on a catalyst $[\text{AuCl}(\text{TPPTS})]$

The development of a technological scheme for the process of catalytic hydration of acetylene on a catalyst $[\text{AuCl}(\text{TPPTS})]$ requires a number of experimental studies related to the industrial implementation of the process, the study of optimal modes, and the selection of the most convenient technological parameters. For this, a pilot plant was developed, taking into account the fact that the reaction of catalytic hydration of acetylene requires the use of gas-liquid reactors. At the same time, at the development stage, it is necessary to take into account the possibility of carrying out the reaction under different hydrodynamic conditions, which can be achieved using the appropriate reactor described in [18]. This reactor, together with the product separation column [19], which makes it possible to effectively isolate the reaction product, acetaldehyde, can be effectively used as part of a single pilot plant. Such a unit can be used for experimental work on the process of catalytic hydration of acetylene using a metal complex homogeneous catalyst [20].

Due to the fact that atmospheric pressure and low temperatures are used both in the gas-liquid reactor and in the product separation column, it becomes possible to use the same type of housings and covers for both apparatuses. Accordingly, when using the same type of parts in both apparatuses, the reinforcement design of the pilot plant also becomes unified, which facilitates the operation and reconfiguration of the unit.

Additionally, it should be noted the need to ensure explosion safety requirements when working with acetylene. All hoses used in the pilot plant are designed exclusively for acetylene service and have bi-directional fire safety valves. In the case when it is not possible to ensure the recirculation of acetylene, the installation provides for the use of its phlegmatization with nitrogen [21], in a ratio of 55 % to 45 %, this mixture is explosion-resistant.

Taking into account the experience gained from the development of a pilot plant, a flow diagram of the process of catalytic hydration of acetylene on the catalyst $[\text{AuCl}(\text{TPPTS})]$ has been developed, shown in Fig. 10.

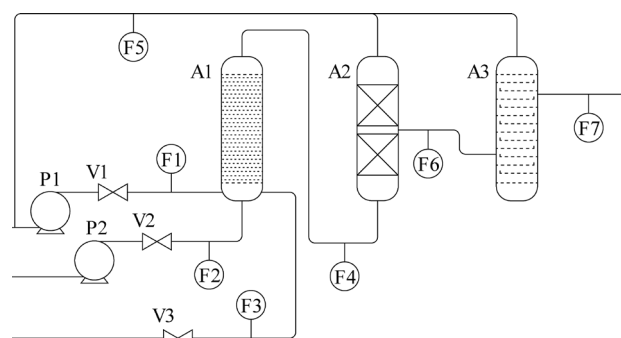


Fig. 10. Technological scheme of the process of catalytic hydration of acetylene on the catalyst $[\text{AuCl}(\text{TPPTS})]$ (the scheme was created using the Visual Paradigm Online Free online service): A1 – gas-liquid reactor; A2 – product separation column; A3 – distillation column; F1 – acetylene flow; F2 – water flow; F3 – catalyst flow; F4 – flow of the reaction mixture; F5 – flow of unreacted acetylene for recirculation; F6 – aqueous solution of acetaldehyde; F7 – purified reaction product, acetaldehyde; P1 – compressor for supplying acetylene; P2 – pump for water supply; V1 – valve regulating the flow of acetylene supply; V2 – valve regulating the flow of water supply; V3 – valve that regulates the flow of catalyst supply

The above diagram shows both the reaction unit, which includes the gas-liquid reactor itself, in which the hydration process takes place, and the product separation column. In this column, acetylene is separated, which has not reacted from the water-acetaldehyde mixture. Later, in the next distillation column, the reaction product, acetaldehyde, is separated from the water-acetaldehyde mixture. The separation of acetaldehyde from a water-acetaldehyde mixture is not energy-consuming, since the boiling point of acetaldehyde at atmospheric pressure is $20.8\text{ }^{\circ}\text{C}$. Separately, it should be noted that the catalyst remains in the reactor all the time during the process. This is possible due to the fact that the process is carried out at a low temperature of $65\text{ }^{\circ}\text{C}$.

6. Discussion of the study of the acetylenes hydration process using a complex of gold chloride as a catalyst

The results obtained make it possible to use the process of hydration of acetylenic compounds using a homogeneous catalyst $[\text{AuCl}(\text{TPPTS})]$ based on gold in the industry of basic organic synthesis. The developed process is carried out at a low temperature of $65\text{ }^{\circ}\text{C}$ and at atmospheric pressure, in contrast to other similar processes, such as the Wacker process. In addition, unlike the process based on the Kucherov reaction, the developed process is more environmentally friendly, since it does not use toxic substances. The organic solvent used, isopropanol, remains in the reactor during the process, since its boiling point is $82.4\text{ }^{\circ}\text{C}$, which is higher than the operating temperature of the process of $65\text{ }^{\circ}\text{C}$. The proposed procedure for obtaining the catalyst itself $[\text{AuCl}(\text{TPPTS})]$, which uses dispersed Au, is also environmentally friendly, and the subsequent preparation of the intermediate complex $[\text{AuCl}(\text{CH}_3)_2\text{S}]$ is carried out by reacting Au with dimethyl sulfoxide. Therefore, the obtained results of the study can be applied to solve the actual problem of developing a modern energy-saving and environmentally friendly process for the

hydration of acetylene compounds. This goal is achieved by the results of solving the tasks:

1) development and practical implementation of an improved method for obtaining a catalyst [AuCl(TPPTS)] based on gold, with sodium salt of triphenylphosphine trisulfonic acid as a ligand and a chlorine atom as a counterion. The catalyst was prepared in a laboratory unit shown in Fig. 1. Improvement concerns the use of dispersed Au with subsequent preparation of the intermediate complex [AuCl(CH₃)₂S] by its interaction with dimethyl sulfoxide. This way of catalyst synthesis [AuCl(TPPTS)] is more environmentally friendly and energy saving. This can be explained by the use of dimethyl sulfoxide in the improved technique. Unlike previous methods that use tetrahydrothiophene, the use of dimethyl sulfoxide is more convenient and safe. A limitation of the modernized method is its three-stage nature. But, at the same time, since almost no catalyst costs occur during the process, the three-stage way of its production is not a problem in its application;

2) development of an effective technique for conducting a kinetic experiment on the hydration of acetylene compounds using phenylacetylene. In particular, the developed method provides for the processing of aliquots by adding them to water and dichloromethane, followed by separation of the organic layer and drying it with Na₂SO₄, filtration and careful evaporation. The resulting mixture is sampled on a ¹H NMR spectrum in CDCl₃, an example of which for a time stamp of 10 min is shown in Fig. 6, which allows to fairly accurately establish the conversion of phenylacetylene, the values of which for other time readings are given in Table. 1. The success of obtaining the results can be explained by the fact that the chosen method of processing aliquots is carried out under mild conditions using the laboratory unit shown in Fig. 3. Due to the limitations of the technique, it is necessary to accurately maintain the temperature regime during the processing of aliquots, which can be implemented without problems using modern measuring technology;

3) determination of the rate constant of the hydration reaction of acetylenic compounds using the example of phenylacetylene on the catalyst [AuCl(TPPTS)]. The result obtained can be explained by the fact that phenylacetylene is an analog of acetylene, but is more convenient and safe due to the liquid state of aggregation, unlike acetylene, which is gaseous. To conduct an experiment to determine the reaction rate constant, a laboratory unit was used, shown in Fig. 2. A limitation of this method is the need for a different hardware design when switching to work with acetylene, which is a gas. But for such a transition, an appropriate set of equipment has been developed, which greatly simplifies such a transition;

4) development of the technological scheme shown in Fig. 10 provides the basis for the commercialization of this process for the production of acetaldehyde. The focus of the study on the application of its results in industry is the advantage of this study compared to similar known ones. This can be explained by the fact that the process allows the catalytic hydration of acetylenes with a high level of conversion at a low temperature at atmospheric pressure. It is also possible to use isopropanol as a solvent in the process. The advantage of using isopropanol is its higher boiling point (82.4 °C) compared to methanol (64.7 °C), which significantly reduces solvent side evaporation, leaving it in the reactor and facilitating the isolation of the reaction product. Unlike the process based on the Kucherov reaction, which uses toxic Hg²⁺ salts, the used catalyst [AuCl(TPPTS)] is

not toxic. A limitation of the process is the use of isopropanol instead of methanol, which, although less toxic, still remains an organic solvent. A way to solve this problem can be the use of ionic liquids instead of organic solvents in the process of further improvement. Thus, the solutions obtained improve the environmental friendliness and energy saving of the process of catalytic hydration of acetylene compounds. Among the shortcomings of the developed process, it should be noted the need to cool water to 8–10 °C before it is fed to the inlet of the reaction product separation column. But at the same time, it should be noted that such cooling is not energy-consuming.

Further development consists in improving the catalyst by synthesizing new complexes based on gold, but with other ligands, possibly also based on phosphorus (III). An important direction of development is the further improvement of the catalytic system, for which it is planned to investigate the possibility of using instead of a low-toxic organic solvent ionic liquids belonging to the so-called “green solvents” and more consistent with the principles of green chemistry. Also, an important direction in the development of the developed process is the further improvement of the hardware design of the process and, in particular, that part of it that is associated with the separation of the finished product from the solvent and reagents that have not fully reacted. In this direction, it is important to make the most of the recycling of reagents in order to build a completely closed production process, which is possible.

7. Conclusions

1. The catalyst [AuCl(TPPTS)], which is a complex of gold chloride, is obtained by an improved method. The catalyst uses the sodium salt of triphenylphosphine trisulfonic acid as a ligand, and the chlorine atom acts as a counterion. The catalyst makes it possible to carry out the process of hydration of acetylenes at a low temperature of 65 °C and at atmospheric pressure.

2. A technique is developed that makes it possible to conduct an experiment to determine the reaction rate constant for the process of hydration of acetylene compounds. The technique makes it possible to carry out an experiment on the example of phenylacetylene and makes it possible to confirm the efficiency of using a homogeneous catalyst [AuCl(TPPTS)], based on the conversion of phenylacetylene.

3. The value of the reaction rate constant $7.3 \pm 0.3 \times 10^{-3} \text{ l/(mols)}$ is determined for the hydration reaction of acetylene compounds. The reaction rate constant is determined based on the catalytic hydration of phenylacetylene using a homogeneous metal complex catalyst [AuCl(TPPTS)]. Aliquots are removed during the reaction to obtain the conversion of phenylacetylene. The process is carried out in methanol/water at a temperature of 65 °C and at atmospheric pressure.

4. A technological scheme of the process of catalytic hydration of acetylene using the catalyst [AuCl(TPPTS)] is developed. Its feature is carrying out the process at a low temperature of 65 °C and at atmospheric pressure. Also, the use of isopropanol, which has a boiling point of 82.4 °C, as a solvent inhibits its evaporation, so that the solvent and catalyst remain in the reactor, facilitating the isolation of the reaction product. These advantages can contribute to the introduction of the developed process in the industry of basic organic synthesis.

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