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STUDY OF THE CATALYTIC REACTION OF HYDRAZINOLYSIS OF ALIPHATIC CARBOXYLIC ACIDS

Abstract. In this work, the reaction of hydrazinolysis of aliphatic carboxylic acid in the presence of an ionite catalyst is considered for the first time. The experiments were made in the static conditions. Previously, the corresponding butyl ether was obtained from the butyric acid, which in interaction with hydrazine formed a hydrazide. The influence of various factors (quantity of hydrazine hydrate, catalyst, butyl alcohol, temperature, reaction duration) on the formation of butyric acid hydrazide was studied. It reveals optimum conditions of synthesis under which the most hydrazide yield made 68%. As a result, the IR spectroscopic researches of the mechanism of hydrazinolysis reaction of the butyl ester of butyric acid with active centers of sulphonic cation-exchange. It is shown that the reaction proceeds with the formation of transition complexes on the surface of the cation exchange resin. The practical value of this work is to develop an effective method of butyric acid hydrazide preparation.

Keywords: butyric acid, hydrazinolysis, hydrazine, hydrazide, catalyst.

Aliphatic carboxylic acid hydrazides and their derivatives are widely used in medical practice, in various sectors of the national economy [1]. For example, 3- hydroxyl- 4,4,4-trichloro butyric acid hydrazide has been proposed for use as a biologically active compound.

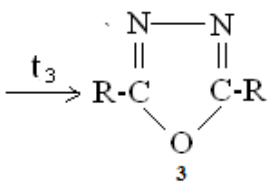
There are various methods of obtaining hydrazides of aliphatic acids. For example, the most promising way to produce hydrazides is the hydrazinolysis of esters, mainly methyl or ethyl esters of the corresponding carboxylic acids, when heated in a solvent medium. For example, 3 - hydroxy-4,4,4-trichlorobutyric acid hydrazide is obtained in an alcohol medium by the reaction of β- trichloromethyl - β-propiolactone with hydrazine hydrate [2].

In addition, methods are known based on the thermal decomposition of carboxylic acid salts with hydrazine [3]. The main patterns that appear when aliphatic carboxylic acids are heated with hydrazine hydrate are generally known and are depicted by the scheme:

$$2RCOOH \xrightarrow{2N_2H_4 \cdot H_2O} [2RCOOH \cdot N_2H_4 \cdot H_2O] \xrightarrow{t_1}$$

$$2RCONHNH_2 + 4H_2O \xrightarrow{t_2} RCONHNHCOR + N_2H_4$$

1 **2**



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The disadvantage of these methods is that, especially when using acids with radicals R> C_3H_7, along with the main product (**1**), are obtained incommensurate amounts of impurities - 1,2-diacylhydrazines (**2**)

and cyclic compounds (**3**). The yield of the main product is increased, in particular, by azeotropic distillation of water. There is also known a method for producing hydrazides by thermal decomposition of $RCONHNH_2 \cdot N_2H_4$ salts (where R = pyrid-4-yl, Ph or lower alkyl) by reacting carboxylic acid (CA) and hydrazine hydrate (HH) with a ratio CA: HH = 1: (1.2 -1.4), in the presence of a catalyst (Al_2O_3, sulfonic cation exchanger) with azeotropic distillation of water [4]. The method is suitable only for lower carboxylic and aromatic acids. Also known is a method of producing hydrazides by thermal decomposition of salts of carboxylic acids with hydrazine hydrate, including mixing carboxylic acid and hydrazine hydrate in a molar ratio of CA: HH = 1: 1.2, heating under reflux in the presence of butanol, active aluminum oxide and benzene, distilling water as an azeotrope at a temperature of 95 °C for 2-8 hours, filtering the melt of the reaction mixture, crystallization, washing and drying the product in vacuum [5]. The yield of hydrazides is 80-95%.

The disadvantage of this method is that it is suitable for obtaining only hydrazides of lower carboxylic aliphatic acids with the radicals R = CH_3, i-C_3H_7. In addition, this method uses solvents that deteriorate the organoleptic properties of the product, which requires additional purification of the target product.

At present, the synthesis of carboxylic acids and their derivatives using heterogeneous catalysts - ionites is the most promising method. In this regard, the synthesis of practically important aliphatic hydrazides in the presence of heterogeneous catalysts is an important task.

The purpose of this study is to investigate the hydrazinolysis of butyl ester in the presence of the sulfonic acid cation exchanger KU-2-8 in the H-form.

Experimental part

Experiments are carried out in static conditions. In a three-neck round-bottom flask with a capacity of 250 ml, equipped with a reflux condenser, 1 g (0.011 mol) of butyric acid, 0.5 g (0.005 mol) of sulfuric acid, 0.9 g (0.012 mol) of butyl alcohol are introduced. The reaction mixture is heated at 90 ° C for 3 hours. Upon completion of the reaction, the mixture is cooled and neutralized with 50 ml of 5% sodium hydrogen carbonate solution. The ether layer is separated and distilled. The butyric acid butyl ester obtained, with a boiling point of 165-166 ° C, is used to further obtaining the corresponding hydrazide.

In a three-neck round-bottom flask with a capacity of 250 ml, equipped with a mechanical stirrer, a thermometer and a reflux condenser, 1 g (0.007 mol) of butyl butyric ester, 0.6 g (0.012 mol) of hydrazine hydrate, 0.67 g of cation exchanger KU-2-8 in H -form, 0.6 g (0.008 mol) of butyl alcohol are introduced. The reaction mixture is heated on a water bath, stirring for 3 hours at a temperature of 80°C. After this time, the mixture is cooled and the cation exchanger is filtered off from the liquid part, washed with 1 ml of butyl alcohol. The alcohol is distilled off from the solution, the remaining solid residue is dried at 30°C. The analysis of butyric acid hydrazide is carried out by the photocolorimetric method. The melting point of hydrazide is 46-49°C. The IR spectra of the starting materials and reaction products are taken on "Impact 410" spectrometer (USA).

Results and their discussion

Butyric acid butyl ester is synthesized by reacting butyric acid and butyl alcohol in the presence of concentrated sulfuric acid.

$CH_3CH_2CH_2COOH+C_4H_9OH \rightarrow CH_3CH_2CH_2COOC_4H_9+H_2O$

The optimal reaction conditions for the esterification of butyric acid are the mass ratio of butyric acid: butyl alcohol: sulfuric acid 1: 0.9: 0.5, temperature of 90°C, 3 hours of reaction time. The yield of butyric ester was 70% of the theoretical.

The IR spectrum, boiling point, and the refractive index of butyl acid butyl ester correspond to those of a standard substance. The resulting ester was used to synthesize butyric acid hydrazide.

Butyric acid butyl ester hydrazinolysis was investigated in the presence of cation exchanger KU-2-8 in the H-form.

$$CH_3CH_2CH_2COOC_4H_9 + N_2H_4 \xrightarrow{KU\text{-}2\text{-}8(H)} CH_3CH_2CH_2CONHNH_2 + C_4H_9OH$$

Under the conditions studied, the main product of the interaction of butyric acid butyl ester with hydrazine hydrate is butyric acid hydrazide. The influence of various factors (the amount of hydrazine

hydrate and cation exchanger, temperature and duration of the reaction) on the formation of hydrazide are given in the table. During hydrazinolysis of butyl acid butyl ester, the optimum process conditions are the mass ratio ester: hydrazine hydrate : butyl alcohol: cation exchanger = 1: 0.6: 0.6: 0.67, temperature of 80°C, 3 hours of reaction time, while the hydrazide yield amounted to 68%.

Table - Butyric acid butyl ester hydrazinolysis (ester mass is 1 g).

hydrazine hydrate, g	cation exchanger, g	butyl alcohol, g	reaction time, hours	temperature, °C	the hydrazide yield, %
0,6	0,67	0,6	3	80	68
0,6	0,67	0,6	3	40	15
0,4	0,67	0,6	3	80	30
0,5	0,67	0,6	3	80	25
0,8	0,67	0,6	3	80	18
0,6	1,00	0,6	3	80	47
0,6	0,67	0,6	2	80	36
0,6	0,67	1,0	3	80	53

In the infrared spectrum of butyric hydrazide, absorption bands of valence vibrations are observed in the region of 1689 cm^{-1} (C = O), 2946– 2863 cm^{-1} (CH, CH_2, CH_3), 1470-1351 cm^{-1} (C – C), 3440 cm^{-1} (NH) groups, as well as deformation vibrations in the region of 1559 cm^{-1} (NH) groups (figure).

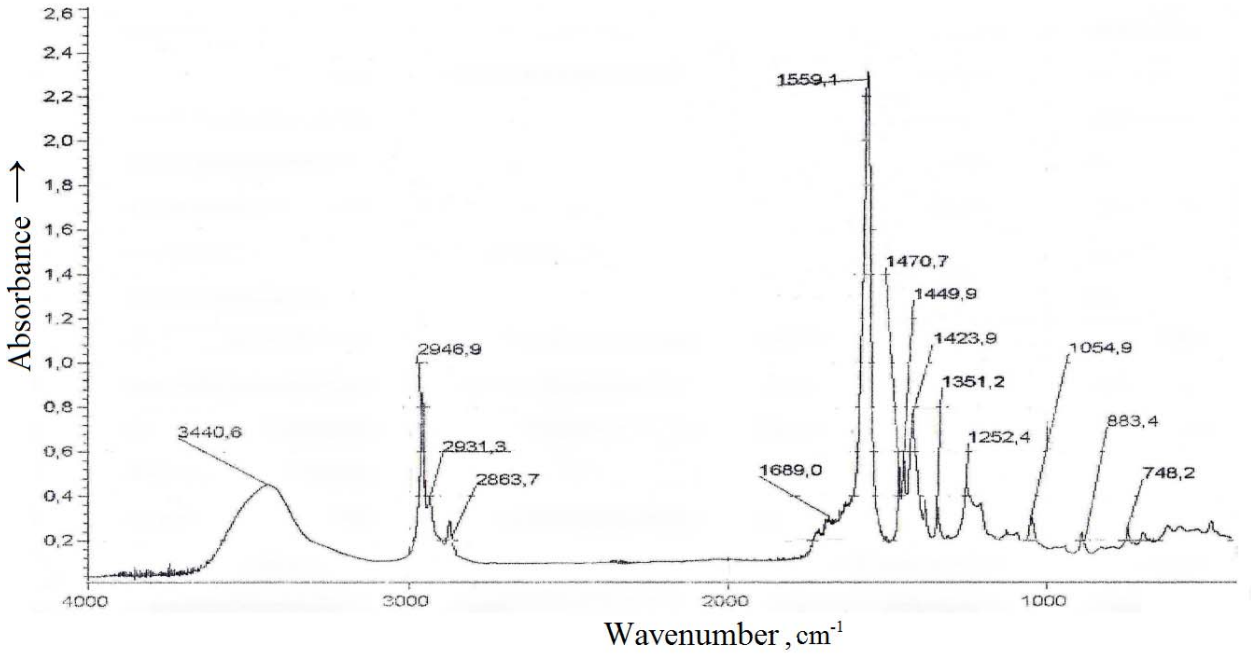
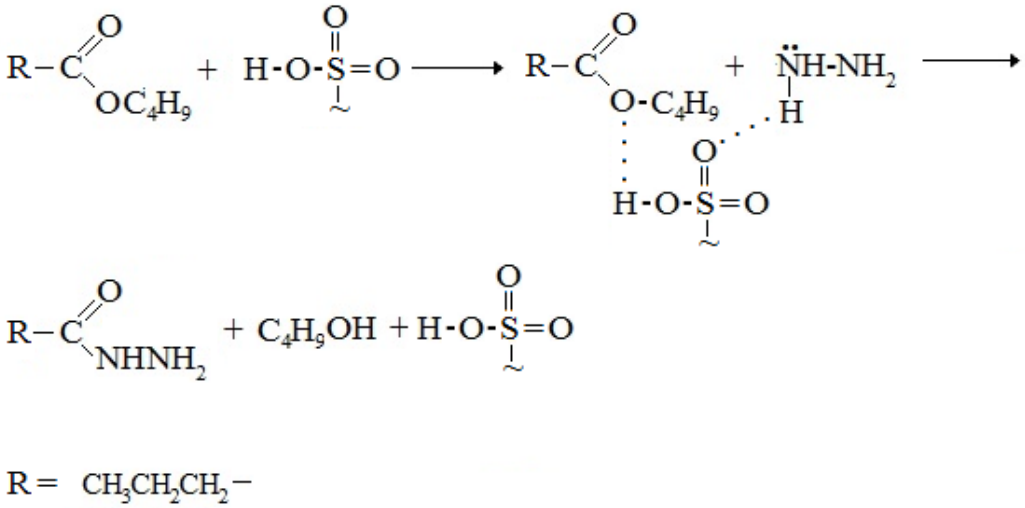


Figure - IR spectrum of butyric acid hydrazide

The mechanism of hydrazinolysis of esters of aliphatic carboxylic acids is still not well understood. According to [7], it can be assumed that hydrazinolysis of butyric acid butyl ester in the presence of an ion exchange resin KU-2-8 (H) is carried out by heterogeneous catalysis and the active centers of the cation exchanger are polymer-bound sulfogroup and hydrogen ions. During the adsorption of butyl ester of butyric acid on sulfonic cation, an intermediate complex is formed, which then interacts with hydrazine to form hydrazide and regenerate the active centers of the ion exchanger.



Thus, we first studied the hydrazinolysis of aliphatic acid esters using the example of butyl acid butyl ester in the presence of KU-2-8 (H) sulfonic cation exchanger, found the optimal process conditions and made conclusions regarding the reaction mechanism.

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АЛИФАТТЫ КАРБОН ҚЫШҚЫЛДАРЫНЫҢ КАТАЛИТТІК ГИДРАЗИНОЛИЗ РЕАКЦИЯСЫН ЗЕРТТЕУ

Аннотация. Бұл жұмыста алғаш рет алифатты карбон қышқылының гидразинолиз реакциясы ионитті катализатор қатысында қарастырылды. Тәжірибелер статикалық жағдайда жүргізілді. Май қышқылынан алдымен оған сәйкес бутилді эфир алынды, ары қарай оны гидразинмен әрекеттестіргенде гидразид түзілді. Май қышқылы гидразидінің түзілуіне әртүрлі факторлардың (гидразингидраттың, катализатордың, бутил спиртінің мөлшері, температура, реакция ұзақтығы) әсері зерттелді. Синтездің оңтайлы жағдайларында май қышқылы гидразидінің шығымы 68 % болды. ИҚ-спектроскопиялық зерттеулер нәтижесінде май қышқылы бутил эфирінің гидразинолиз реакциясы сульфокатионниттің активті орталықтарының қатысуымен жүзеге асатын механизмі ұсынылды. Реакцияның катионит бетінде ауыспалы комплекстердің түзілуімен жүретіндігі көрсетілді. Бұл жұмыстың практикалық маңыздылығы май қышқылының гидразидін алудың тиімді әдісін ойластыру болып табылады.

Түйін сөздер: май қышқылы, гидразинолиз, гидразин, гидразид, катализатор.

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ИССЛЕДОВАНИЕ КАТАЛИТИЧЕСКОЙ РЕАКЦИИ ГИДРАЗИНОЛИЗА АЛИФАТИЧЕСКИХ КАРБОНОВЫХ КИСЛОТ

Аннотация. В этой работе впервые рассмотрена реакция гидразинолиза алифатической карбоновой кислоты в присутствии ионитного катализатора. Опыты проводили в статических условиях. Предварительно из масляной кислоты был получен соответствующий ему бутиловый эфир, который при взаимодействии с гидразином образовал гидразид. Изучено влияние различных факторов (количества гидразингидрата, катализатора, бутилового спирта, температуры, продолжительности реакции) на образование гидразида

масляной кислоты. В оптимальных условиях синтеза выход гидразида масляной кислоты составил 68 %. В результате ИК- спектроскопических исследований предложен механизм реакции гидразинолиза бутилового эфира масляной кислоты с участием активных центров сульфокатионита. Показано, что реакция протекает с образованием переходных комплексов на поверхности катионита. Практическая значимость работы состоит в разработке наиболее эффективного способа получения гидразида масляной кислоты.

Ключевые слова: масляная кислота, гидразинолиз, гидразин, гидразид, катализатор.

REFERENCES

[1] Ioffe B.V., Kuznetsov M.A., Potekhin A.A. Chemistry of organic derivatives of hydrazine. L.: Himiya, 1979. 224 p. (in Russ.).

[2] Colla V.E., Berdinsky I.S. Pharmacology and chemistry of derivatives of hydrazine. Joshkar-Ola: Mariyskiy book edition, 1976. 264 p. (in Russ.).

[3] Auth. Certificate № 1054775/23-4. USSR. The way of receiving hydrazides 3- oksi-4,4,4- trichlorobutyric acid Luknitsky F.I., Vovsi B.A. Issue Date : 14.01.1967 (in Russ.).

[4] Patent № 2147020 Russian Federation . The method of obtaining hydrazides of aliphatic carboxylic acids and their mixtures. / A.G. Drozdetsky, A.V.Radushev , A.S.Turbin , et. al. Issue Date : 03.27.2000 (in Russ.).

[5] Dzhumadullaeva S.A., Altynbekova M.O. A Mechanism for the Hydrazinolysis of Benzoic Acid in the Presence of Ion-exchange Catalyst // Russian Journal of Physical Chemistry A. **2013.** V.787. № 11. P. 1943-1945 (in Eng.).

[6] Dzhumadullaeva S.A., Baeshov A.B. Ion-Exchange Resin Catalysts in the Liquid-Phase Hydrazinolysis of Cinnamic Acid. // Kinetics and Catalysis. **2017.** V. 58. № 1. P. 24. (in Eng.).

[7] Dzhumadullaeva S.A., Baeshov A.B. Reaction of hydrazinolysis of oxalic acid at presence of sulfonic acid cation exchanger. // Reports of the NAS RK. **-2017.** V. 6. № 426. P.87- 91 (in Kaz.).

[8] Tsundel G. Hydration and intermolecular interaction. Investigation of polyelectrolytes by infrared spectroscopy. M.: Mir, 1969. 310 p. (in Russ.).

[9] Semushin A.M., Yakovlev V.A., Ivanova E.V. Infrared absorption spectra of ion-exchange materials. L .: Himiya, Leningradskoe otdelenie, 1980. 96 p. (in Russ.).

[10] Gragerov I.P., Pogorelyy V.K., Franchuk I.F. Hydrogen connection and fast proton exchange. Kiev: Naukova Dumka, 1978. 215 p. (in Russ.).

[11] Bayeshov A.B., Myrzabekov B.E., Kolesnikov A.V. PATTERNS OF FORMATION OF DISPERSED COPPER POWDERS IN THE BODY OF ELECTROLYTE DURING THE USE OF COPPER ANODE IN SULFURIC ACID SOLUTION ALONG WITH TITANIUM (IV) IONSN E W S OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN SERIES CHEMISTRY AND TECHNOLOGY ISSN 2224-5286 https://doi.org/10.32014/2018.2518-1491.31 Volume 6, Number 432 (2018), 96 – 101.

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