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Sveta A. Dzhumadullaeva[1*], Abduali B. Baeshov[2]

[1]*Khoja Akhmet Yassawi International Kazakh-Turkish University, Kazakhstan;*
[2]*D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry, Almaty, Kazakhstan*
*(*Corresponding autor 's e-mail: sveta.jumadullayeva@ayu.edu.kz)*

An Efficient Ion-Exchange Resin Catalysts for the Liquid-Phase Selective Hydrazinolysis of Succinic Acid

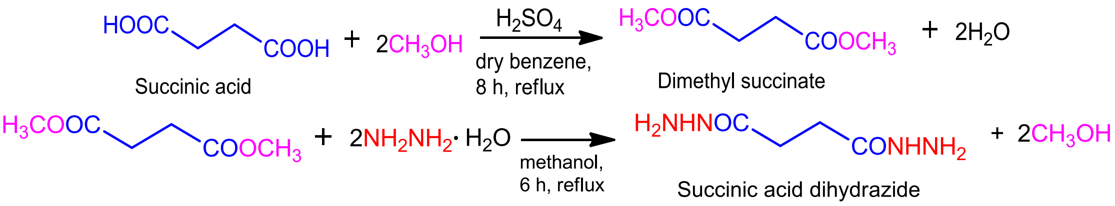
Dicarboxylic acid dihydrazides are widely used as pharmaceutical intermediates, plant growth regulators, water-based coating additives, epoxy crosslinking agents. Dihydrazides are prepared by adding hydrazine hydrate to an acid halides and diesters. In this work the hydrazinolysis of succinic acid was studied using various ion exchange resins as catalysts, and the optimum conditions and the reaction mechanism were identified. Analysis of the initial reagents and the target product were performed out using photocolorimetric and IR spectroscopic methods, the composition of the target product was determined by elemental analysis. Hydrazinolysis of succinic acid were performed in aqueous medium in the temperature 90 °C for 3 h. Succinic acid conversion was 82–95 %, and the succiniyldihydrazide yield 61–93 %. It has been shown the efficient catalysts for the hydrazinolysis of succinic acid are AV-17-8, AN-31 and AN-1 anion exchangers. The highest succinyldihydrazide yield (93 %) was obtained with anion exchanger AV-17-8. On the basis of IR spectroscopic studies, a plausible process mechanism was suggested. A probable mechanism of the process with the formation of supramolecular complexes with the participation of substrates and fixed polymer-bound quaternary ammonium and hydroxyl ions of the anion exchanger was proposed. Thus, the most efficient method of succinic acid dihydrazide preparation has been proposed in comparison with known methods.

Keywords: succinic acid dihydrazide, hydrazinolysis, heterogenious catalyst, ion exchange resins, supramolecular complexes.

Introduction

Hydrazide derivatives of dicarboxylic acids are widely used as drugs with antimicrobial, antifungal, antibacterial, and antitubercular activity [1–6]. Among the substituted hydrazides of succinic acid, compounds with hypoglycemic and hypertensive effects were found [7]. Metal dihydrazide complex compounds as ecologycally safe chemical compounds are applied in agriculture as efficient plant growth regulating chemicals [8]. For example, succinic acid 2,2-dimethylhydrazide (Daminoside) is a well known compound used as an active ingredient in plant growth regulating compositions [9, 10]. Dihydrazides are added to the composition of epoxy in varnishes and nickel corrosion inhibitors [11, 12]. Succinyldihydrazide is water-based coating additive, epoxy crosslinking agent, aldehyde remover, textile additive and biochemical reagent, which can be mainly used in laboratory organic synthesis process and chemical and pharmaceutical production research and development process [1–5, 11]. Many dihydrazides are used to recover metal ions from industrial waste water as reagents to form anti-corrosive metal coatings [13].

The preparation of dihydrazides from the corresponding dicarboxylic acids did not give the desired results, so they were synthesized by hydrazinolysis of various derivatives of dicarboxylic acids (acid halides and anhydrides, diesters) in medium of organic solvents [3, 14]. According to this method [15], the obtaining succinyldihydrazide is carried out through the esterification of corresponding acid using concentrated sulfuric acid, followed hydrazinolysis of the resulting dimethyl succinate in methanol (Sheme 1):



Scheme 1. Synthesis of dimethyl succinate under acid catalysis conditions and hydrazinolysis of dimethyl succinate

The synthesis of dimethyl succinate is demanding process. The reaction is carried out in large excess of absolute methanol (therefore, its absoluization is necessary, which requires the expenditure of electricity and reagents). The use of sulfuric acid as a catalyst experiences strong corrosivity, large environmental hazard, complex side reaction, low yield and the like. Second reaction step — hydrazinolysis of dimethyl succinate also has certain disadvantages: hydrazine hydrate concentration used in the method is 10 times of that of esters, the general reaction time is up to 14 hours, and the yield of succinicdihydrazide is only 89 %.

Therefore, the search for an efficient method for preparing of dihydrazides with low production cost, high conversion rate and few side reactions is an urgent problem.

We have previously shown the possibility of using some cation exchange resins as catalysts for the hydrazinolysis of oxalic and maleic acids with yields of the corresponding hydrazides of 63 and 90 % [16]. Using kinetic and IR spectroscopic studies, a probable mechanism of the process was proposed that involved hydrogen ions of the polymer catalyst. However, there is no information in the literature about the use and catalytic properties of ion exchangers in the synthesis of other dihydrazides and about the reaction mechanism. Compared with inorganic catalysts, ion exchange resins exhibit excellent catalytic performance and are easily regenerated. The use of a solid ion exchange resin as catalyst has a number of advantages: the catalyst is easily separated from the reaction products, does not require neutralization and concentration, has high selectivity with respect to the target product, can be used many times after appropriate processing, and does not corrode the industrial equipment.

As a continuation of work on the exploration of novel heterogenious catalysts for the preparation of acid dihydrazides, in the present paper was studied the reaction between succinic acid and aqueous hydrazine in the presence of ion exchanger catalysts, and also identified the optimum conditions and the probable reaction mechanism using the IR spectroscopic method.

Experimental

Materials and Methods

For preparation of succinic acid dihydrazide, commercial hydrazine hydrate and succinic acid used were reagent grade without further purification. Hydrazine hydrate (purity 99.9 %) was provided by Ural Industrial Chemical Plant, Russia. Succinic acid (chemically pure) was provided by ChemBio Service, Russia. The solvents were purified and absolutized according to standard methods. The following commercial ion exchange resin were used as catalysts: hyghly basic anion exchanger AV-17-8 (grain size 0.4–0.6 mm), weakly basic anion exchangers AN-31 (0.4–2.0 mm) and AN-1 (0.4–2.0 mm), strongly acidic sulfonic acid cation exchanger KU-2-8 (0.40–0.55 mm), and phosphoric acid cation exchanger KRF-10 P (0.5–1.0 mm), produced by Olaine Chemical Plant Biolar, Latvia. They were conditioned and converted into the H^+/OH^- form by a standard method [17]. The exchange capacity of ion exchangers was measured under static conditions by a standard method [18]. Exchange capacity of the ion exchanger, mg-equiv/g: AV-17-8 — 4.2; AN-31 — 3.8; AN-1 — 3.6; KU-2-8 — 3.0; KRF-10P — 3.2.

C, H and N elemental analyses were performed with a X-Calibur elemental analyzer (Xenemetrix Ltd, Israel). The photocolorimetric analyses of succinic acid and corresponding dihydrazide were carried out on a Fluorat-02-5M device (Lumex, Russia) [19]. The course of reactions and the purity of the target product were monitored by TLC on Merck Silica gel 60G F254 plates. IR spectroscopic studies of initial reagents and the reaction product have been carried out on an Impact-410 FT-IR spectrometer (Nicolet, USA) as KBr pellets in the 4000–400 cm^{-1} region.

General Procedure for the Preparation of Succinic acid Dihydrazide

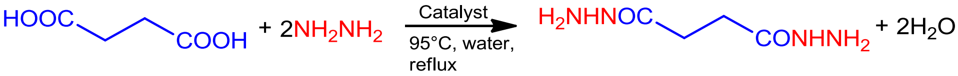
Succinic acid (0.85 mmol), hydrazine hydrate (1.5–2.6 mmol) and 1.0–2.5 g an air-dry polymer catalyst were mixed and heated in 8–20 ml of water for 1.5–4.0 h at 90 °C. Then, the final mixture was cooled and the catalyst was separated by filtration. The aqueous solution was evaporated, and the dry residue was recristallized from absolute ethanol.

Yield: 93 % , m.p. 169–173 °C. IR (KBr, ν, cm^{-1}): 3180, 3205, 3298, 3318, 1575, 1537 (N–H), 1632 (C=O), 1185, 1124, 1089 (C–N), 2880, 2928, 2966, 2651, 1461, 1423, 1396 (C–H),1295, 1273, 1240, 664 (CH_2), 953, 925 (N–N), cm^{-1}. Elemental analysis: Found, %: C, 32.85; H, 6.82; N, 38.33. $C_4H_{10}N_4O_2$. Calculated, %: C, 32.84; H, 6.84; N, 38.32.

Results and Discussion

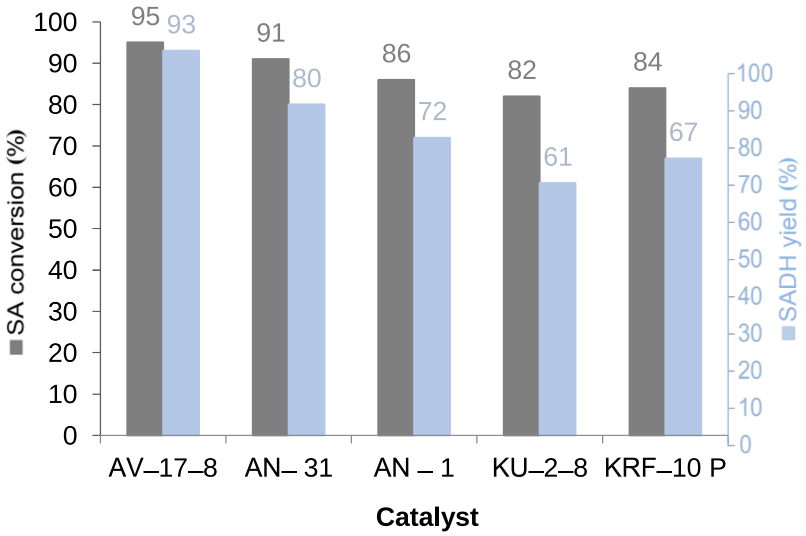
Chemistry. Investigation of Catalytic Activity

We found that succinic acid (SA) readily reacted with hydrazine hydrate (HH) on the catalyst, to yield succinyldihydrazide (SADH) (Scheme 2):



Scheme 2 Synthesis of succinic acid dihydrazide

In addition to succinyldihydrazide, monohydrazide succinic acid ($HOOCCH_2CH_2CONHNH_2$) was obtained in small quantities. All tested catalysts are active in this process: the conversion of SA is 82–95 %, and the SADH yield is 61–93 % (Fig. 1). The highest SADH yield (72–93 %) with a SA-to-dihydrazide conversion selectivity of 96–97.4 % is obtained with AV-17-8, AN-31 and AN-1. However, the polymer catalysts KU-2-8 and KRF-10P, which have the properties of solid acids, did not show sufficient activity in the process under study.



Reaction conditions: SA:HH:Catalyst:H_2O mass ratio of 1:0.82:2:8, 90 °C, 3 h

Figure 1. Comparison of the catalytic activity of ion exchangers in the reaction succinic acid with hydrazine*

In addition to being composition and structure dependend, the catalytic properties of the ion exangers are strongly influenced by the operating conditions. When studying the influence of various factors (duration of the experiment, concentration of substrates and catalyst) on the process, it was found that in the case of using AV-17-8 (OH), the yield of SADH reaches 93 % (Table). The optimal conditions for preparation SADH from SA at 90 °C were identified: contact time 3 h, SA:HH:Catalyst:H_2O mass ratios of 1:0.82:2:8.

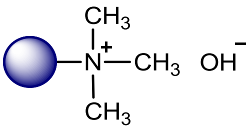
Table

SADH synthesis over the catalyst AV-17-8 (OH) at 90 °C

SA:HH:Cat:H_2O	Time, h	SADH yield,%	SA:HH:Cat:H_2O	Time, h	SADH yield, %
1:0.84:2:8	1.5	59	1:0.76:2:8	3.0	73
1:0.84:2:8	2.5	82	1:1.05:2:8	3.0	90
1:0.84:2:8	3.0	93	1:1.34:2:8	3.0	89
1:0.84:2:8	4.0	89	1:0.84:2:8	2.0	68
1:0.84:1.0:8	3.0	64	1:0.84:2:10	3.0	91
1:0.84:1.5:8	3.0	80	1:0.84:2:12	3.0	85
1:0.84:2.5:8	3.0	83	1:0.84:2:20	3.0	82

IR Spectroscopy. Proposed Reaction Mechanism

Basing on the reference information it could be suggested that hydrazinolysis of SA on the catalyst AV-17-8 (OH) ion-exchange resin occurred via a heterogeneous catalytic mechanism in which the polymerbound quaternary ammonium ions and OH ions are responsible for the process [20] (Sheme 3):



Sheme 3. The active site of catalyst AV-17-8 (OH)

Depending on the nature of the active center of the ion exchanger, non-covalent interaction (electrostatic, hydrogen bonding, Van der Waals forces) can occur, resulting in the formation of supramolecules – complex associates consisting of two or more molecules held together by intermolecular forces. Based on the data on the IR spectra of the AV-17-8 anion exchanger after interaction with succinic acid and hydrazine, various aggregate supramolecular complexes of adsorbed molecules with active centers of the ion-exchange resin were found [21].

In the spectrum characterizing the interactions of succinic acid with AV-17-8 (OH), there is no very intence absorbtion bands at 1739 cm^{-1} that is due to the stretching vibrations of the C=O group and an absorbtion band at 907 cm^{-1} assigned to the out-of-plane deformation vibration of the OH group of succinic acid (Fig. 2).

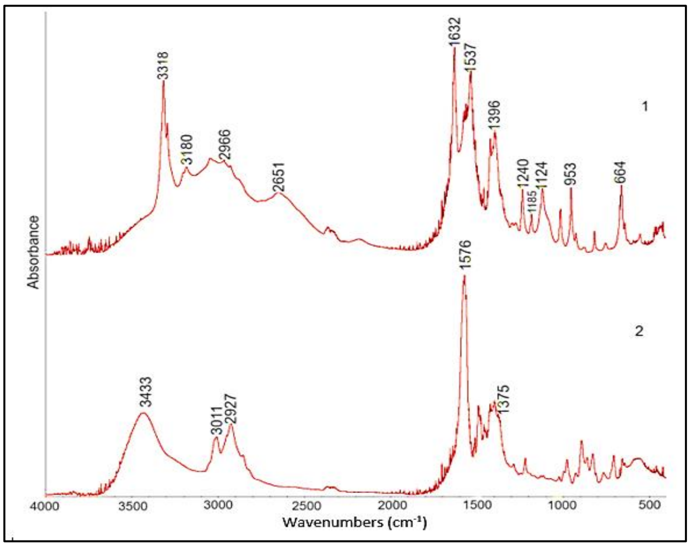
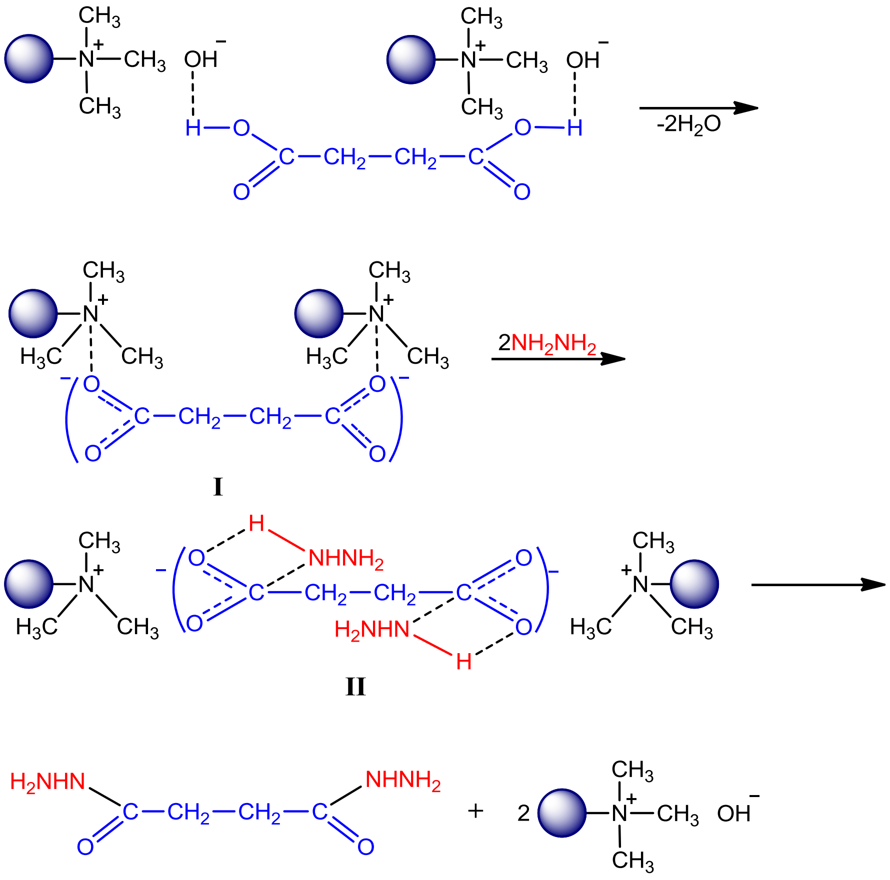


Figure 2. IR absorbtion spectra of (1) succinic dihydrazide
and (2) the interaction product of succinic acid with the catalyst

In the range of 3800–2500 cm^{-1}, a broad, intense band with maxima at 3433, 3011 and 2927 cm^{-1} is observed, the bands with frequencies of 2927, 2880, 1421 and 1398 cm^{-1} refer to the stretching and bending vibrations of the C–H groups. It was found that the adsorbtion of succinic acid is carried out due to yield a hydrogen bond with hydroxyl groups located on the surface of the catalyst [22]. Along with the characteristic anion exchanger bands, intense absorbtion bands at 1375 and 1576 cm^{-1} appear, which can be assigned to symmetric and antisymmetric vibrations of the carboxylat group — COO^{-} which became the counterions of the fixed cations of the resin (intermediate **I**). Consequently, the carboxylate anion-catalyst complex decomposes under the action of hydrazine to yield the intermediate **II**, wich is converted to the desired dihydrazide with subsequent regeneration of the active site (Sheme 4):



Scheme 4. Proposed mechanism for the synthesis of SADH on the AV-17-8 (OH) as catalyst

Similar IR spectroscopic and kinetic evidences supporting the formation of adsorbtion complexes under the conditions of interfacial catalysis established during alkylation of different benzyl amines, ketones in an aqueous medium, catalyzed by quaternary ammonium salts, and reaction of oleic acid with hydrazine on the polymer catalyst [20, 23, 24].

Reusability of the Catalyst

After the reaction completion, the polymer catalyst AV-17-8 is treated with an aqueous-alcoholic solution, which washes out the dihydrazide adsorbed on the ion exchanger surface, then it is regenerated with a 10 % of NaOH solution. As a result, the ion exchanger operation life considerably increases, and the catalyst preserves the initial activity and selectivity for a long time.

Conclusions

In summary, we have proposed a one-step method for obtaining of succinic acid dihydrazide using a novel heterogeneous, efficient and reusable ion-exchange catalysts. It established that the most efficient catalysts for the selective hydrazinolysis of succinic acid are basic anion exchangers AV-17-8 and AN-31. The conversion of succinic acid was 91–95 %, and yield of SADH was 80–93 %. Conditions were determined for the catalytic synthesis of SADH on anion exchanger AV-17-8 (OH) in aqueous medium, which provided yields of SADH as high as 93 %. A probable mechanism of the reaction with the participation of fixed ammonium ions and counterions of the anion exchanger was proposed on the basis of results from IR spectroscopic studies. The polymer catalyst AV-17-8 used can be easily recovered and reused without a significant decrease in the yield of the product. The proposed one-step method offers several advantages: high selectivity of the process with respect to the target product, repeated use of a catalyst, no need for anticorrosion equipment and organic solvents, environmental safety compared to known methods for synthesis of dihydrazides, therefore the method can be useful and attractive for preparation of succinyldihydrazide.

*Author Information**

**The authors' names are presented in the following order: First Name, Middle Name and Last Name*

Sveta Absadykovna Dzhumadullaeva (*corresponding author*) — Candidate of Chemical Sciences, Professor of the Khoja Akhmet Yassawi International Kazakh-Turkish University, B. Sattarchanov avenue, 29, 160200, Turkestan, Kazakhstan; e-mail: sveta.jumadullayeva@ayu.edu.kz; https://orcid.org/0000-0003-2673-2915

Abduali Baeshovich Baeshov — Doctor of Chemical Sciences, Academician of the National Academy of Sciences of the Republic Kazakhstan, D.V. Sokolsky Institute of Fuel,Catalysis and Electrochemistry, Kunaev street, 142, 050010, Almaty, Kazakhstan; e-mail: bayeshov@mail.ru; https://orcid.org/0000-0003-0745-039X

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: **Sveta Absadykovna Dzhumadullaeva** conceptualization, data curation, investigation, methodology, validation, visualization, writing-review & editing; **Abduali Baeshovich Baeshov** conceptualization, formal analysis, visualization, resources, supervision, validation, writing-review & editing.

Conflicts of Interest

The authors declare no conflict of interest.

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