# Ion-Exchange Resin Catalysts in the Liquid-Phase Hydrazinolysis of Cinnamic Acid

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Abstracts—The catalytic activity of a synthetic ion-exchange resins has been studied in the reaction of cinnamic acid with hydrazine (aqueous medium, 363 K, 1.0-2.5 h) yielding the corresponding hydrazide. Efficient catalysts for the process are the anion-exchange resins AV-17-8 and AN-31. The modifying effect of the substrate—hydrazine hydrate—on the catalytic properties of the ion-exchange systems has been demonstrated. On the basis of IR spectroscopic studies, a plausible process mechanism was suggested. It involves polymer-bound quaternary ammonium ions of the anion exchanger.

*Keywords:* ion-exchange resin catalysts, liquid-phase hydrazinolysis, cinnamic acid **DOI:** 10.1134/S0023158417010025

Interest in synthetic derivatives of cinnamic acid is caused by the possibility of synthesizing, on their basis, antituberculosis and hepatoprotective drugs and antioxidants. [1]. For example, cinnamic acid hydrazide is active against Mycobacterium tuberculosis. It provides a basis for the synthesis of a number of other physiologically active substances [2]. For this reason, methods for the synthesis of cinnamic acid derivatives have been extensively studied, particularly the hydrazinolysis reaction of carboxylic acids and their esters. Cinnamic acid hydrazide was synthesized [3] by cinnamic acid esterification followed by the hydrazinolysis of the ester in absolute ethanol. However, disadvantages of this method are the low yield of cinnamic acid hydrazide (55%) and the necessity of employing solvents that can impair the organoleptic properties of the product. Because of the latter circumstance, the product needs to be additionally purified.

The hydrazinolysis of carboxylic acids in an aqueous medium by the action of a basic catalyst is more promising, for it allows obtaining hydrazides of aromatic and heterocyclic carboxylic acids in a single step. We have demonstrated the possibility of using ion exchange resins and synthetic zeolites as catalysts for hydrazinolysis of 4-cyanopyridine and benzoic acid in the synthesis of the corresponding hydrazides [4, 5].

Ion-exchange resin catalysts based on styrenedivinylbenzene copolymers have several advantages: they are very selective, allow the reaction to be conducted under relatively mild conditions, are easily separable from the reaction mixture (which allows a continuous process.) do not require neutralization or concentration, and enable one to avoid high water consumption and equipment corrosion.

The aim of this work was to study the catalytic activity of a number of synthetic ion-exchange resins in the reaction between cinnamic acid and aqueous hydrazine and to optimize the reaction conditions.

### **EXPERIMENTAL**

The following commercial synthetic ion exchange resins were used as catalysts: highly 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 (0.45-0.50 mm), strongly acidic sulfonic acid cation-exchange resin KU-2-8 (0.40-0.55 mm), and phosphoric acid cation exchanger KRF-10P (0.5-1.0 mm). They were conditioned and converted into H<sup>+</sup>/OH<sup>-</sup>-form by a standard method [6]. The exchange capacity of the ion exchangers was measured under static conditions by a standard method [7].

Cinnamic acid hydrazide was synthesized from cinnamic acid by reacting it with hydrazine hydrate in the presence of an ion-exchange resin catalyst. Experiments were carried out in a static system in a temperature-controlled 250-cm<sup>3</sup> glass reactor equipped with a mechanical stirrer, thermometer, and reflux condenser using commercial hydrazine hydrate (99.9%) and cinnamic acid (reagent grade). The reaction mixture, which consisted of cinnamic acid, hydrazine hydrate, water and an air-dry ion exchanger, was heated in a water bath at 363 K for 1–2.5 h. Next, the mixture was cooled and the ion exchanger was filtered out. The aqueous phase was evaporated to dryness at

Catalyst	Exchange capacity of the ion exchanger, mg-equiv/g	CA conversion, %	CAH yield, %
AV-17-8	4.2	94	90
AN-31	3.8	92	78
AN-1	3.6	87	74
KU-2-8	3.0	80	62
KRF-10P	3.2	82	69

Table 1. Cinnamic acid hydrazinolysis over the ion-exchange resin catalysts\*

\* Reaction conditions: CA : HH : Cat :  $H_2O = 1 : 0.72 : 2 : 16, 363 \text{ K}, 2 \text{ h}.$ 

Table 2. CAH synthesis over the anion exchanger AV-17-8(OH<sup>-</sup>) (363 K)

$CA : HH : Cat : H_2O$	Time, h	CAH yield, %	$CA : HH : Cat : H_2O$	Time, h	CAH yield, %
1: 0.72: 2: 161: 0.72: 2: 161: 0.72: 2: 161: 0.72: 2: 161: 0.72: 2: 161: 0.72: 0.5: 16	1.0 1.5 2.5 2.0 2.0	56 63 87 90 68	1: 0.60: 2: 161: 0.80: 2: 161: 1.10: 2: 161: 0.72: 2: 81: 0.72: 2: 10	2.0 2.0 2.0 2.0 2.0 2.0	76 87 78 64 69
1:0.72:1.0:16 1:0.72:1.5:16	2.0 2.0	82 85	$1: 0.72: 2: 12 \\ 1: 0.72: 2: 20$	2.0 2.0	81 89

333 K. The dry residue was recrystallized from absolute ethanol. The resulting hydrazide had a melting point of 373–374 K. Its composition was determined by elemental analysis. For  $C_9H_{10}N_2O$  calcd., %: C, 66.59; H, 6.16; N, 17.26. Found, %: C, 66.35; H, 6.27; N, 17.39. IR spectrum, v, cm<sup>-1</sup>: 1693 (C=O), 1541 (CH=CH), 3210, 3340 (N–H), 3027 (C–H)<sub>Ar</sub>, 1182 (C–N), and 989 (N–N).

The reaction was monitored using photocolorimetric analysis [8]. The IR spectra of the starting materials and the reaction product (in KBr pellets) were recorded on an Impact-410 spectrometer (Melles Griot, United States) in the 400-4000 cm<sup>-1</sup> range.

## **RESULTS AND DISCUSSION**

Under the conditions examined, the main product of the reaction between cinnamic acid (CA) and hydrazine hydrate (HH) is cinnamic acid hydrazide (CAH).

$$C_{6}H_{5}CH=CHCOOH + NH_{2}-NH_{2}$$

$$\xrightarrow{C_{at}} C_{6}H_{5}CH=CHCONHNH_{2} + H_{2}O.$$

As can be seen from Table 1, all tested catalysts are active in this process: the conversion of CA is 80-94%, and the CAH yield is 62-90%. The highest CAH yield (78-90%) with a CA-to-hydrazide conversion selectivity of 84-95% is obtained with AV-17-8 and AN-31 (Table 1). AN-1 is slightly inferior to them. On passing from the highly basic anion exchanger AV-17-8 to the acidic cation exchangers KU-2-8 and KRF-10P, the catalytic activity and selectivity decrease considerably.

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The introduction of hydrazine hydrate, a strong base, to the reaction mixture smoothes the catalytic action of ion exchangers with different acid—base properties. According to the literature [9], in acid—base catalysis the reaction medium can change the degree of hydration and the strength of acid sites and the proportions of Lewis and Brønsted sites, thus altering the character of the processes. In our case, the modifying effect of the substrate (hydrazine hydrate) shows itself most clearly: the acidic ion exchangers KU-2-8 and CRF-10P acquire the ability to accelerate the reaction, which typically occurs in the presence of a basic catalyst.

In addition to being composition- and structuredependent, the activity and selectivity of the ion exchangers are strongly influenced by the operating conditions. For AV-17-8 in OH<sup>-</sup> form, depending on the contact time, on the proportions of the reactants, and on the amount of catalyst, the CAH yield ranges from 56 to 90% of the theoretical yield (Table 2). It was found that the optimal conditions for the synthesis of the hydrazide at 363 K are the following: duration, 2 h; CA : HH : Cat : H<sub>2</sub>O weight ratios of 1 : 0.72 : 2 : 16.

The literature [10] suggests that the cinnamic acid hydrazinolysis reaction in the presence of ion exchange resin AV-17-8 (OH<sup>-</sup>) proceeds via a heterogeneous catalytic mechanism in which the polymerbound quaternary ammonium ions and hydroxyl ions are responsible for the process:

$$(CH_3)_3N^+OH^- \xleftarrow{} (CH_3)_3N^+ + OH^-.$$

The adsorption of cinnamic acid on the anionexchange resin results in the formation of carboxylate anions, which block the fixed groups of the resin according to the following scheme:

$$C_{6}H_{5}-CH = CH - C \bigvee_{OH}^{O} + N^{+}(CH_{3})_{3}OH^{-} \cdot nH_{2}O$$

$$\longrightarrow \begin{bmatrix} C_{6}H_{5}-CH = CH - C & O \\ & O \end{bmatrix}^{-} N^{+}(CH_{3})_{3} \cdot (n+1)H_{2}O$$

In the spectrum characterizing the interactions of cinnamic acid with AV-17-8 (OH), there is no very intense absorption bands at ~ 1643 cm<sup>-1</sup> that is due to the stretching vibrations of the C=O group of cinnamic acid. Against the background of the own bands of the anion exchanger (figure), intense absorption bands at 1396 and 1689 cm<sup>-1</sup> appear, which can be assigned to symmetric and antisymmetric vibrations of the carboxylate group  $-COO^{-}$  [11].

The IR spectrum of the anion exchanger that is in contact with hydrazine hydrate practically does not differ from the spectrum of the initial anion exchanger, indicating that there is no adsorption of hydrazine. Consequently, the carboxylate anion-catalyst complex decomposes under the action of hydrazine from the reaction medium bulk to yield the desired hydrazide, regenerating the active site.

$$\begin{bmatrix} C_{6}H_{5}-CH=CH-C & O \\ O \end{bmatrix}^{-} N^{+}(CH_{3})_{3} \cdot (n+1)H_{2}O$$

$$\xrightarrow{NH_{2}-NH_{2} \cdot H_{2}O} C_{6}H_{5}-CH=CH-C & O \\ NHNH_{2} + N^{+}(CH_{3})_{3}OH^{-} \cdot nH_{2}O.$$

A similar mechanism was proposed in the case of catalysis of benzoic acid hydrazinolysis by AV-17-8 in  $OH^-$  form [5]. Consequently, for the liquid-phase

hydrazinolysis of cinnamic acid over a catalyst with basic sites (anion-exchange resin), a similar reaction mechanism can be expected.

#### **CONCLUSIONS**

The most effective catalysts for the selective hydrazinolysis of cinnamic acid are the ion exchange resins with basic properties, namely, AB-17-8 and AN-31. Over these catalysts, the cinnamic acid conversion is 92-94% and the CAH yield is 78-90%. The modifying effect of hydrazine hydrate was demonstrated in the case of the acidic catalysts KU-2-8 and KRF-10P. The catalytic cinnamic acid hydrazide synthesis conditions ensuring 56-90% hydrazide yield for the anion exchanger AV-17-8(OH<sup>-</sup>) in an aqueous medium were found. A plausible hydrazinolysis mechanism over the anion exchanger was suggested on the basis of IR spectroscopic studies. This mechanism involves polymerbound quaternary ammonium ions.

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