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## SHORT COMMUNICATIONS

# A Mechanism for the Hydrazinolysis of Benzoic Acid in the Presence of Ion-exchange Catalyst

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Abstract—A mechanism for the hydrazinolysis of benzoic acid via cyclic transition states is proposed on the basis of kinetic and IR spectroscopic studies.

*Keywords*: hydrazinolysis, benzoic acid, hydrazine hydrate, anion exchange resin, benzhydrazide, adsorption, active site, fixed cation of resin.

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## INTRODUCTION

The hydrazinolysis of carboxylic acids over polymeric ion exchange resin catalysts is a promising method for synthesizing aromatic and pyridinecarboxylic acid hydrazides, which are used as drugs, accelerators of rubber vulcanization, modifiers, and curing agents for polymeric materials. However, there is no clear idea of the mechanism of the hydrazinolysis reaction [1]. In this work, we attempt to fill this gap by investigating hydrazinolysis of benzoic acid into benzhydrazide in the presence of AV-17-8 anion exchange resin.

#### **RESULTS AND DISCUSSION**

Our investigations were performed by kinetic means and IR spectroscopy. The experimental procedure was described in [2, 3].

We found that benzoic acid reacts quite readily with hydrazine to form benzhydrazide (BH) in the presence of AV-17-8 anion exchange resin in the OH-form:

$$C_6H_5COOH + H_2N - NH_2$$
  
 $\rightarrow C_6H_5CONHNH_2 + H_2O_2$ 

The dependence of the BH concentration (*c*) on time at various temperatures is shown in Fig. 1. The reaction rate constants at 65, 75, 80, and 95°C are  $2.9 \times 10^{-3}$ ,  $3.0 \times 10^{-3}$ , and  $4.2 \times 10^{-3}$  L/(mol min), respectively. The activation energy found from the Arrhenius dependence was 20.1 kJ/mol. The entropy of activation, calculated using the method in [4], was -198.2 J/(mol K). At different initial concentrations of benzoic acid ( $c_0 = 0.10$ , 0.30, and 0.51 mol/L), the

rate constants were  $0.25 \times 10^{-3}$ ,  $2.8 \times 10^{-3}$ ,  $2.9 \times 10^{-3}$  L/(mol min), respectively. The order of the reaction with respect to benzoic acid was 1 (Fig. 1). It was similarly established that the reaction was of the first order with respect to the second component, hydrazine hydrate (HH). For HH concentrations  $c_0' = 0.81$ , 0.93, and 1.06 mol/L, the rate constant values were  $2.9 \times 10^{-3}$ ,  $3.0 \times 10^{-3}$ ,  $3.1 \times 10^{-3}$  L/(mol min).

The low activation energy, the high negative entropy of activation, and the first order with respect to benzoic acid and hydrazine hydrate indicate that the reaction occurs via a cyclic transition state. These kinetic data are consistent with the results from IR spectroscopic studies.

The spectra of benzoic acid (1) and the product of its interaction with the anion exchange resin (2), respectively, are shown in Fig. 2. Comparing them to each other, we can see there are no absorption bands that are characteristic of acids (the very strong stretching vibration band of the C=O group at 1700  $cm^{-1}$  and the absorption band at 940 cm<sup>-1</sup> referring to the out-ofplane deformation vibration of the OH-group) in the spectrum 2. The continuous absorption characteristic of both acid and the anion exchange resin disappeared. The intensity of the band in the region of deformation vibrations of water  $(1600-1700 \text{ cm}^{-1})$  is reduced dramatically. At the same time, a very intense pair of bands at 1370 and 1615 cm<sup>-1</sup> appeared for the reaction product of benzoic acid with anion exchange resin. This pair of bands can be attributed, respectively, to the symmetric stretching vibrations of carboxylate anions (COO<sup>-</sup>), which become fixed counterions of the resin according to [5, 6]:

$$\mathbb{R} - \mathbb{C} \bigvee_{OH}^{O} + \mathbb{N}^{+} (CH_{3})_{3}OH^{-} \cdot H_{2}O \longrightarrow \mathbb{R} \mathbb{C} \bigvee_{O}^{O} \left| \begin{array}{c} \mathbb{N}^{+} (CH_{3})_{3} + 2H_{2}O \\ \mathbb{I} \\ \mathbb{I} \\ \end{array} \right|$$



**Fig. 1.** Kinetics of the hydrazinolysis of benzoic acid over AB-17-8 anion exchange resin: (a) at  $c_0 = 0.51$  M,  $c_0 = 0.81$  M,  $K_T = 2$  g/g BH and different temperatures: (1) 65, (2) 75, (3) 80, and (4) 95°C; (b) at 95°C,  $c_0 = 1.6$  M and different values of  $c_0$ : (1) 0.51, (2) 0.30, and (3) 0.10 M.



Fig. 2. IR absorption spectra of benzoic acid (1) and the product of its interaction with AB-17-8 anion exchange resin in OH-form (2), respectively.

The IR spectrum of the anion exchange resin upon contact with hydrazine hydrate does not differ from the spectrum of the fresh anion exchange resin, indicating there was no adsorption of hydrazine. We may therefore assume that the complex of carboxylate anion with the catalyst decomposes under the action of hydrazine from the reaction volume, leading to the formation of the target hydrazide and the regeneration of the active site:

$$\begin{array}{c|c} RC & O \\ H_2N-HN & O \\ H \end{array} \begin{array}{|c|c|} -N^+(CH_3)_3 \longrightarrow RC & + & N^+(CH_3)_3OH^-. \\ NHNH_2 & \downarrow \\ & & \\ \end{array}$$

CONCLUSIONS A plausible mechanism of hydrazinolysis of carboxylic acids over an anion exchange resin thus involves the formation of the cyclic transition state.

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