

Catalytic Hydrogenation of Cinnamic Acid and Salicylic Acid

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Hydrogenation of cinnamic acid and salicylic acid was carried out using 5 %Ru/C, 5 % Pd/C and Ru-Sn/Al₂O₃ catalyst at 493 K and 6.89 MPa of hydrogen partial pressure. Ru-Sn/Al₂O₃ catalyst was found to be active for hydrogenation -COOH group to give cinnamyl alcohol. The selectivity to cinnamyl alcohol was low (15 %) as absolute inhibition of C=C bond hydrogenation in cinnamic acid is challenging. 5 %Pd/C catalyst was found to hydrogenate C=C bond and aromatic ring in cinnamic acid. 5 %Ru/C catalyst was found to be least selective catalyst as it hydrogenated C=C bond, aromatic ring and -COOH group in cinnamic acid. Hydrogenation of salicylic acid is not possible at 493 K as decarboxylation of salicylic acid occurs.

Keywords: Hydrogenation, Cinnamic acid, Chemoselectivity, Ru-Sn/Al₂O₃.

INTRODUCTION

The organic compounds which can be hydrogenated are alkenes, alkynes, aliphatic aldehydes and ketones, aromatic aldehydes and ketones, sugars, esters, anhydrides and carboxylic acids, nitriles and nitro compounds [1]. Compared to hydrogenation of nitro, aromatic ring, aldehyde, and ketonic functional groups, hydrogenation of carboxylic acids largely entails extreme reaction conditions like high temperature and high hydrogen pressure [2]. Different types of selectivity observed for hydrogenation reactions are chemoselectivity, regioselectivity, stereoselectivity and enantioselectivity [3]. The activation energy for hydrogenation of various functional groups is different and also dependent on the steric surroundings nearby the functional group [4]. For unsaturated carboxylic acids, it is difficult to selectively reduce carboxylic group in the presence of a C=C bond as the activation energy for hydrogenation of C=C is lower as compared to -COOH group [3]. In organic moieties where C=C is not conjugated with the carbonyl group, discriminate hydrogenation of carbonyl group to the unsaturated alcohol takes place without difficulty, particularly when the double bond is highly substituted, similar study for hydrogenation of substituted cinnamic acids has also been reported [5,6]. Hydrogenation C=C double bond in cinnamic acid is investigated but selective hydrogenation of -COOH group is not deeply studied [7]. Hydrogenation of -COOH, C=O & C=C groups are well investigated individually for different compounds like acetylene, ethylene, aldehydes, ketone and succinic acid. Hydrogenating C=O bond in carboxylic acid is tough relative to aldehyde and ketone [8]. Similarly hydrogenation of C=C is rapid in case of alkene than benzene. Chemo-selective hydrogenation of -COOH group in presence of aromatic ring is studied for benzoic acid, phthalic acid, isophthalic acid and terephthalic acid [9,10].

In this article, we have carried out hydrogenation of cinnamic acid and salicylic acid. Cinnamic acid has -COOH group, C=C bond & aromatic ring available for hydrogenation whereas salicylic acid has -COOH and aromatic ring. Here study related to hydrogenation of cinnamic acid was carried out to understand the selectivity of Pd, Ru & Ru-Sn catalyst for different functional groups present in cinnamic acid. Hydrogenation of salicylic acid was carried to observe hydrogenation of -COOH, aromatic ring and hydrogenolysis of -OH group present in salicylic acid. Hydrogenolysis of salicylic acid is considered here as hydrogenolysis of -OH is reported in literature [11]. Product distribution for hydrogenation of cinnamic acid and salicylic acid with Ru, Pd and Ru-Sn based catalyst is also reported in this article.

EXPERIMENTAL

Salicylic acid, cinnamic acid, metal salt precursors like PdCl₂, RuCl₃·H₂O, ReCl₃·2H₂O and CoCl₂·6H₂O were obtained from S.D. Fine Chemicals, India. The 5 % Ru/C and 5 % Pd/C catalysts were obtained from Arora Matthey Ltd., India. The reaction medium (1,4-dioxane) of analytical reagent-grade was obtained from Merck India Ltd., Mumbai, India

Catalyst preparation: The catalysts Ru-Sn/Al₂O₃ was prepared by impregnation method followed by calcination and reduction. The details of catalyst preparation method is reported by Shinde and Deshpande [12] for kinetics of benzoic acid.

Reactor set-up and experimental procedure for high pressure reactions: The reactions were performed in a reactor supplied by Parr Instruments Co. USA designed for severe reaction conditions. Experimental procedure followed for hydrogenation of cinnamic and salicylic acid is same as reported for other organic carboxylic acids [12].

GC-MS analysis: The products for hydrogenation of cinnamic acid and salicylic acid were ascertained by using GC-MS. Quantification was accomplished by using gas chromatography (Agilent Systems 6890 GC) equipped with HP Chemstation software. For separation of reduction products, a HP INNOWax column was utilized. For quantification of hydrogenation products calibration was done by external standard method [13]. Quantitative analysis of cinnamic acid and salicylic acid was done by esterification method as reported for hydrogenation of dicarboxylic acids [10].

RESULTS AND DISCUSSION

Hydrogenation of cinnamic acid with 5 % Ru/C, 5 % Pd/C and 5 % Ru-29 % Sn/Al₂O₃ catalyst: Hydrogenation of

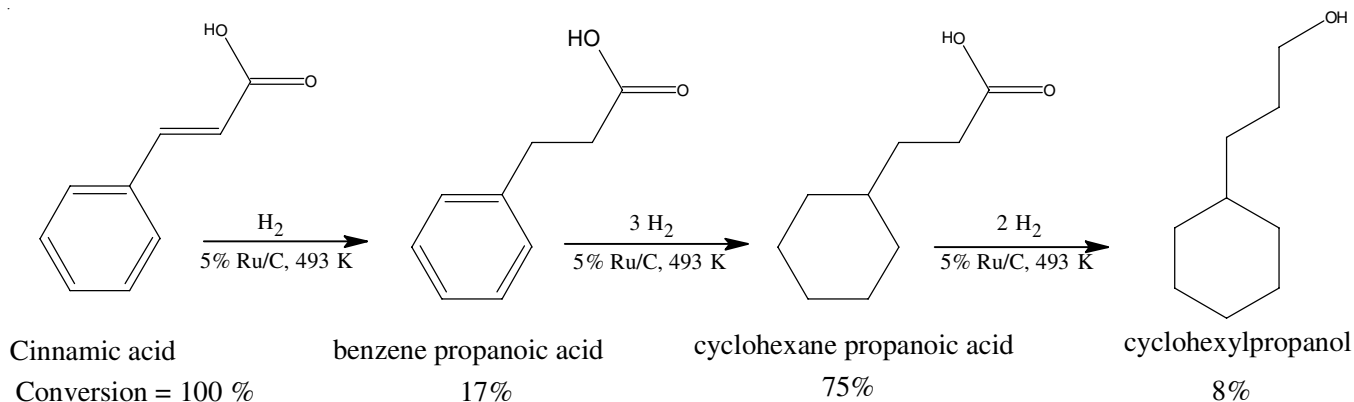
cinnamic was carried out at 493 K, 6.89 MPa of hydrogen partial pressure and catalyst concentration of 5 kg/m³. The concentration of cinnamic acid in 1,4-dioxane was 0.82 kmol/m³. The total volume for the hydrogenation reaction was 2.5 × 10⁻⁵ m³.

Hydrogenation of cinnamic acid with 5 % Ru/C catalyst gives benzene propanoic acid, cyclohexane propanoic acid and 3-cyclohexyl propanol at the end of 6 h. Conversion of cinnamic acid was 100 % and selectivity to benzene propanoic acid, 3-cyclohexane propanoic acid and 3-cyclohexyl propanol was 17, 75 and 8 %, respectively. The reaction pathway for hydrogenation of cinnamic acid with 5 % Ru/C catalyst is shown in **Scheme-I**.

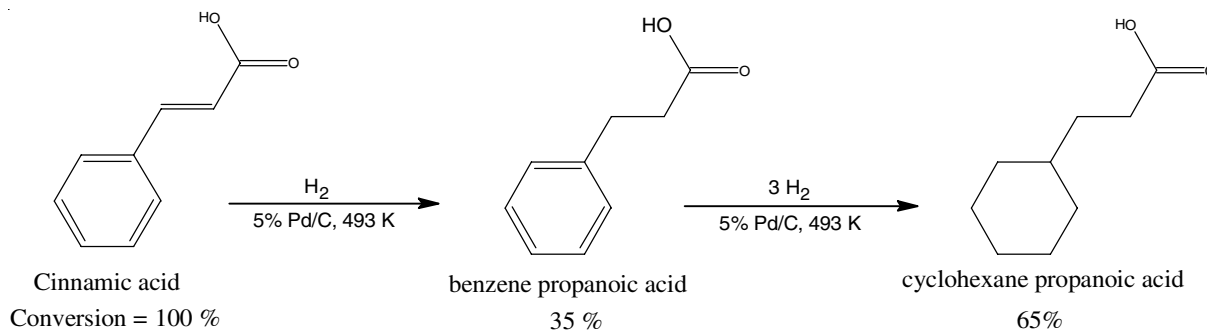
Hydrogenation of cinnamic acid with 5 % Pd/C catalyst gives benzene propanoic acid and cyclohexane propanoic acid as shown in **Scheme-II**. Conversion of cinnamic acid was 100 % with 35 % selectivity to benzene propanoic acid and 65 % selectivity to cyclohexane propanoic acid.

When hydrogenation of cinnamic acid is carried out with Ru-Sn/Al₂O₃ catalyst, hydrogenation of aromatic ring is completely inhibited. A 6 % conversion of cinnamic acid with 85 % selectivity to benzene propanoic acid and 15 % selectivity to cinnamyl alcohol was obtained. The reaction scheme for hydrogenation of cinnamic acid with Ru-Sn/Al₂O₃ catalyst is shown in **Scheme-III**.

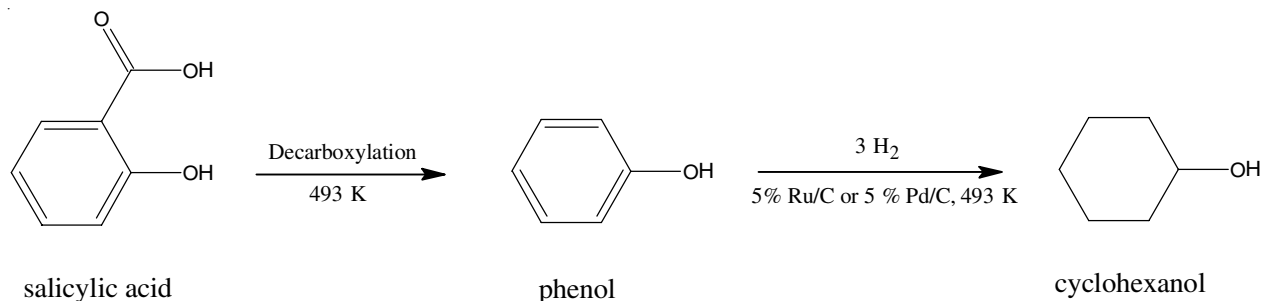
Hydrogenation of salicylic acid with 5 % Ru/C, 5 % Pd/C and 5 % Ru-29 % Sn/Al₂O₃ catalyst: Hydrogenation of salicylic acid was also carried out at 493 K, 6.89 MPa of hydrogen partial pressure and catalyst concentration of 5 kg/m³. The concentration of salicylic acid in 1,4-dioxane was kept 0.82 kmol/m³. The reaction charge volume for hydrogen was 2.5 × 10⁻⁵ m³.



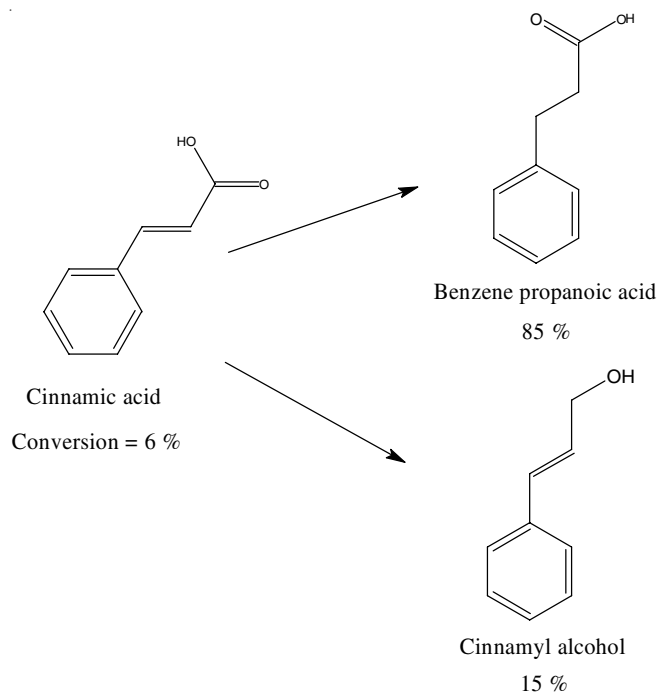
Scheme-I: Hydrogenation of cinnamic acid with 5 % Ru/C catalyst



Scheme-II: Hydrogenation of cinnamic acid with 5 % Pd/C catalyst



Scheme-IV: Hydrogenation of salicylic acid with Ru/C or Pd/C catalyst



Scheme-III: Hydrogenation of cinnamic acid with Ru-Sn/Al₂O₃ catalyst

With 5 % Ru/C and 5 % Pd/C, hydrogenation of carboxylic group of salicylic acid does not occur at 493 K as decarboxylation of carboxylic group takes place to give phenol followed by the hydrogenation of phenol to cyclohexanol (**Scheme-IV**). Ru-Sn/Al₂O₃ catalyst is inactive for hydrogenation of phenol. With 5 % Ru/C catalyst there is a 100 % conversion of phenol to cyclohexanol with total selectivity, whereas with 5 % Pd/C catalyst a 78 % conversion of phenol with 100 % selectivity to cyclohexanol is observed. Hydrogenolysis of -OH group of salicylic acid was not observed under the reaction conditions mentioned above.

Conclusion

Hydrogenation of cinnamic acid with Ru-Sn/Al₂O₃ catalyst was found to give benzene propanoic acid and cinnamyl alcohol. With Ru-Sn/Al₂O₃ catalyst, hydrogenation of aromatic ring did not occur but total inhibition of C=C bond in cinnamic acid not possible. 5 % Pd/C catalyst hydrogenated aromatic ring and C=C bond in cinnamic acid. 5 % Ru/C was found to be active for C=C bond, aromatic ring and -COOH group in cinnamic acid. Hydrogenation of salicylic acid is not possible

because a decarboxylation reaction takes place to give phenol. Hydrogenolysis of phenol doesn't occur with Ru-Sn/Al₂O₃, 5 % Pd/C and 5 % Ru/C catalyst. It is observed that 5 % Pd/C and 5 % Ru/C catalyst were active for hydrogenating aromatic ring in phenol, while Ru-Sn/Al₂O₃ catalyst is inactive for hydrogenation of phenol.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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