



# Synthesis of cinnamyl acetate by solid–liquid phase transfer catalysis: Kinetic study with a batch reactor

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## ABSTRACT

The present study reports the synthesis of cinnamyl acetate (ROAc) from cinnamyl bromide (RBr) and sodium acetate (NaOAc) in a batch reactor using quaternary ammonium bromide (QBr) as a phase transfer catalyst under a solid–liquid reaction mode. The factors affecting the reaction such as kind of catalyst, agitation speed, temperature, amount of catalyst, mole ratio of cinnamyl bromide to sodium acetate, addition of water and particle size of sodium acetate were investigated. The results indicate that the catalyst with longer alkyl chain length gave better performance. The results on effect of agitation speed reveal that the solid–liquid interfacial mass transfer resistance is negligible at agitation speed above 600 rpm. The reaction rate increased with the increase in the temperature and complete conversion of RBr could be obtained within 90 min using a moderate amount of tetra-*n*-butyl ammonium bromide as the catalyst at 95 °C, while 100% selectivity of cinnamyl acetate was observed in all the cases. Adding 1–8 ml of water improved the reactivity of the catalyst and 4 ml was an optimal amount. The use of NaOAc in the form of fine powder showed far better performance than that in the form of 2 mm granules. The reaction results fitted into the pseudo-first order rate equation and the activation energy was found to be 11.2 kcal mol<sup>-1</sup>.

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## 1. Introduction

Phase transfer catalysis (PTC) is a most useful technique for conducting the reaction from two immiscible substrates. It has generated a lot of interest as alternatives for conventional processes due to the possibility of carrying out the reaction at low temperatures and pressures, which enhance the process reliability and flexibility [1–3]. Liquid–liquid PTC involves the reaction of anionic reactant from aqueous phase with the reactant in organic phase by a phase transfer catalyst. It has been successfully employed for the synthesis of fine and specialty chemicals for the last few decades. However, the process suffers from the problem of separation and purifying the final product from the catalyst [4,5]. The major drawback of liquid–liquid PTC in the etherification and esterification reactions is lower selectivity of the product due to the hydrolysis of the products and other side reactions in the aqueous phase. Furthermore, the carboxylic acids shows less reactivity in liquid–liquid PTC. The use of solid–liquid PTC (S–L PTC) eliminates the need of using aqueous phase thus eliminates the separation problems and easy recovery of the catalyst and enhances the product selectivity by avoiding the side reactions. The S–L PTC involves

the reaction between the solid nucleophile with the other reactant in the organic liquid phase. The mechanism and kinetics of solid–liquid PTC was first studied by Yadav and Sharma [6] for the reaction of benzyl chloride with solid sodium acetate. The addition of a little water into the S–L PTC generates a new phase called “omega phase” [6–16] around the solid reactant to enhance the solubilization of the solid and formation of the catalytic intermediate. Naik and Doraiswamy [2] developed a systematic procedure for modeling reactions in S–L PTC. The kinetics and the catalytic behavior of the active intermediate were extensively studied by Yang et al. [14] for the benzylation of sodium salicylate with benzyl bromide in solid–liquid system. Here we focus our efforts on studying the kinetics and factors affecting the synthesis of cinnamyl acetate from cinnamyl bromide and sodium acetate by S–L PTC.

## 2. Experimental

Cinnamyl acetate (98%) and sodium acetate were obtained from Aldrich Chemicals. Tetra-*n*-butyl ammonium bromide was purchased from Fluka Chemicals. Chlorobenzene was procured from Merck Chemicals. A 125 ml three-neck round-bottom flask equipped with a reflux condenser and mechanically agitated stirrer was used as a batch reactor. The reactor was placed in a temperature controlled water bath. Known quantities of sodium acetate (0.025 mol) in the form of fine powder, cinnamyl bromide

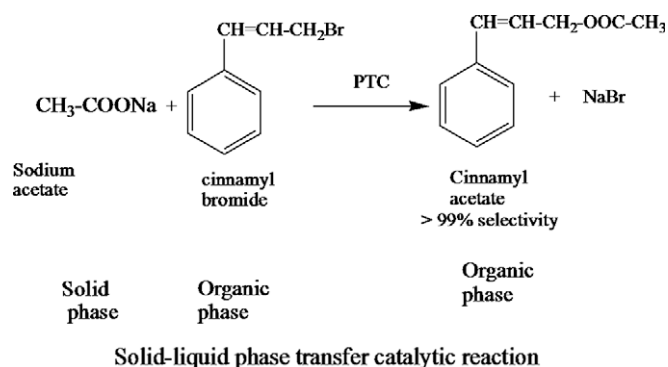
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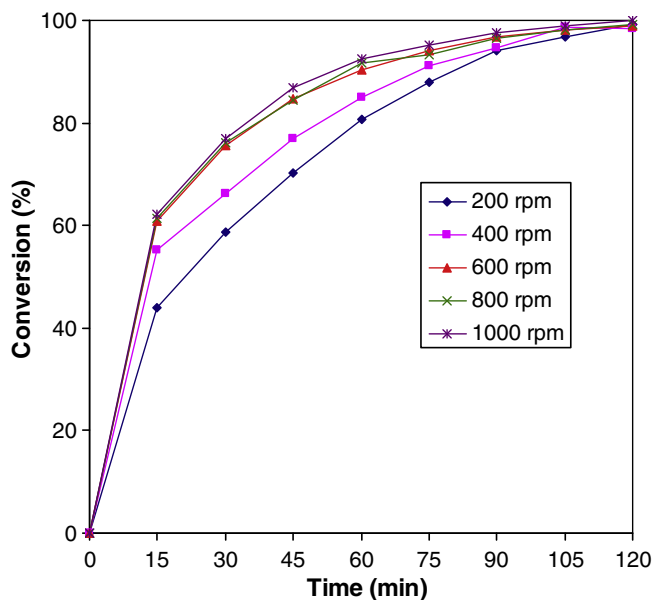
(0.02 mol) and n-dodecane (internal standard) were poured into the reactor, chlorobenzene was added to make up a total volume of 50 mL and the temperature of the solid–liquid mixture was raised to 90 °C with constant stirring. The reaction was started by adding a required amount of phase transfer catalyst when the temperature reached the set value. At preset times, the stirrer was turned off temporarily and 0.5 ml of organic solution was pipetted out and analyzed on a gas chromatograph (Shimadzu GC-14A with FID) using SE-30 Column.

### 3. Results and discussion

The S–L PTC involves the reaction between the Sodium acetate (solid nucleophile) with the other reactant cinnamyl bromide from the organic liquid phase. The schematic representation of the nucleophilic substitution reaction is shown in the following reaction scheme.



In order to optimize the reaction conditions, the esterification reaction was carried out by varying the speed of agitation, type of catalyst, reaction temperature, catalyst loading and concentration of cinnamyl bromide, and the results are discussed in the following sections. Note that sodium acetate used in this study is in the form of fine powder unless otherwise mentioned.



**Fig. 1.** Effect of agitation speed. Cinnamyl bromide, 0.02 mol; sodium acetate, 0.025 mol; catalyst: TBAB; catalyst loading, 1.6 g; chlorobenzene, to make up total volume 50 ml; temperature, 90 °C.

#### 3.1. Effect of agitation speed

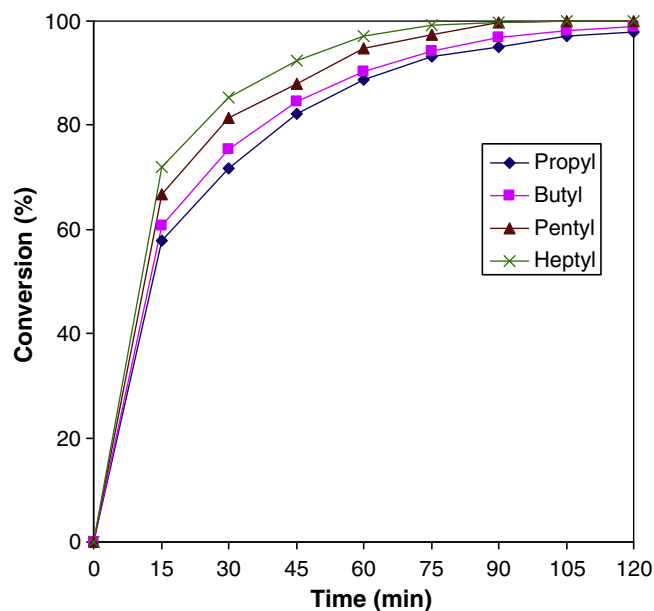
In solid–liquid phase reaction system, the interfacial mass transfer may strongly affect the apparent reaction rate. Increasing the agitation speed might increase the contacting area between and relative velocity of the two phases, and hence diminish the interfacial mass transfer resistance. The reaction was carried out by varying the agitation speed from 200–800 rpm using tetra-*n*-butyl ammonium bromide (TBAB) as a catalyst and the results are shown in Fig. 1. This figure indicates that the conversion of cinnamyl bromide increases with increase of agitation speed from 200 to 600 rpm. However, conversion remains almost constant at agitation speed beyond 600 rpm. This result reveals that the interfacial mass transfer resistance between the solid surface and organic phase is negligible when the agitation speed is above 600 rpm. In this context, agitation speed was fixed at 600 rpm for all further experiments.

#### 3.2. Effect of alkyl chain length of the catalyst

The reaction was carried out with four kinds of tetra-alkyl ammonium bromides, including tetrapropyl ammonium bromide (TPRAB), tetra-*n*-butyl ammonium bromide (TBAB), tetra-*n*-pentyl ammonium bromide (TPEAB), tetra-*n*-heptyl ammonium bromide (THEPAB) catalysts, and the results are depicted in Fig. 2. As it can be seen from Fig. 2, the catalytic activity increased with the increase in alkyl chain length of the catalyst. The catalyst with longer alkyl chain length, tetra-*n*-heptyl ammonium bromide, gave better performance. However, the catalysts with longer alkyl chain length are more easily dissolved in the organic phase and hence are more difficult to be removed and reused after the reaction. Hence TBAB is chosen as the phase transfer catalyst in the following studies.

#### 3.3. Effect of reaction temperature

The effect of reaction temperature on esterification was studied at 80, 85, 90 and 95 °C. The results shown in Fig. 3 indicate that the conversion of cinnamyl bromide increases with the increase in the



**Fig. 2.** Effect of alkyl chain length of tetra-alkyl ammonium bromide. Cinnamyl bromide, 0.02 mol; sodium acetate, 0.025 mol; catalyst loading, 1.6 g; chlorobenzene, to make up total volume 50 ml; temperature, 90 °C; agitation speed, 600 rpm.

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