



Esterification of sodium 4-hydroxybenzoate by ultrasound-assisted solid–liquid phase-transfer catalysis using dual-site phase-transfer catalyst



Hung-Ming Yang*, Wei-Ming Chu

Department of Chemical Engineering, National Chung Hsing University, 250 Kuo-Kuang Road, Taichung 402, Taiwan, ROC

ARTICLE INFO

Article history:

Received 3 April 2013

Received in revised form 29 July 2013

Accepted 5 August 2013

Available online 13 August 2013

Keywords:

Solid–liquid phase-transfer catalysis

Dual-site phase-transfer catalyst

Ultrasound irradiation

Esterification

Benzyl 4-hydroxybenzoate

ABSTRACT

The catalytic esterification of sodium 4-hydroxybenzoate with benzyl bromide by ultrasound-assisted solid–liquid phase-transfer catalysis (U-SLPTC) was investigated using the novel dual-site phase-transfer catalyst 4,4'-bis(tributylammoniomethyl)-1,1'-biphenyl dichloride (BTBAMBC), which was synthesized from the reaction of 4,4'-bis(chloromethyl)-1,1'-biphenyl and tributylamine. Without catalyst and in the absence of water, the product yield at 60 °C was only 0.36% in 30 min of reaction even under ultrasound irradiation (28 kHz/300 W) and 250 rpm of stirring speed. When 1 cm³ of water and 0.5 mmol of BTBAMBC were added, the yield increased to 84.3%. The catalytic intermediate 4,4'-bis(tributylammoniomethyl)-1,1'-biphenyl di-4-hydroxybenzoate was also synthesized to verify the intrinsic reaction which was mainly conducted in the quasi-aqueous phase locating between solid and organic phases. Pseudo-first-order kinetic equation was used to correlate the overall reaction, and the apparent rate coefficient with ultrasound (28 kHz/300 W) was 0.1057 min⁻¹, with 88% higher than that (0.0563 min⁻¹) without ultrasound. The esterification under ultrasonic irradiation using BTBAMBC by solid–liquid phase-transfer catalysis was developed.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Phase-transfer catalysts can conduct the reactions between mutually immiscible reactants under mild conditions. It has been widely applied in manufacturing pharmaceuticals, agricultural chemicals, flavorants, dyes, perfumes and environmental processes, etc [1]. Phase-transfer catalysis (PTC) can be divided into several categories, including liquid–liquid, solid–liquid, gas–liquid, liquid–liquid–solid, and liquid–liquid–liquid types. For solid–liquid phase-transfer catalysis (SLPTC), water is seldom used or only introduced in a very small quantity, thus the hydrolysis side-reaction can be effectively inhibited and the reaction rate can be promoted. SLPTC exhibits the advantages of easy separation of products, easy selection of organic solvents, easy recovery of catalysts and prevention of unfavorable side reactions and behaves as a green technology in organic synthesis [2,3].

In SLPTC, the nucleophile reactant is in solid form and the other reactant exists in the organic solvent [4]. The catalytic intermediate is formed from the reaction of solid reactant and the catalyst dissolving in organic solvent, and transferred into the bulk organic phase to conduct the intrinsic reaction with the organic substrate [5,6]. Hence, the content of the catalytic intermediate in the organic sol-

vent is important to achieve a high catalytic activity. The decay of reaction rate by SLPTC was commonly observed due to the side-product salt deposited on the surface of solid reactant particles, reducing the formation of the catalytic intermediate [7,8]. The way to remove the deposited side-product from the surface of particles during the progress of reaction is also important to gain a favorable product synthesis by SLPTC. Recently, in PTC, multi-site phase-transfer catalyst shows significant enhancement in reaction rate [9]. Multi-site phase-transfer catalyst contains more than one active center, and has the potential to be used in solid–liquid system.

Ultrasonic irradiation in liquid–liquid phases can increase interfacial area coupled with local hot-spot generation, and has been demonstrated to promote high reaction rate in organic synthesis [10–13]. Under ultrasonic irradiation, the liquid jet could be favorable to employ for removing the surface-deposited side-product in SLPTC and increasing the formation of the catalytic intermediate.

Ultrasound irradiation combined with liquid–liquid PTC has revealed significant improvement in the reaction rate. In third-liquid PTC system, the overall reaction rate can also be effectively raised by ultrasound in two-phase flow reactor [14] or with dual-site phase-transfer catalyst [15,16]. But the application of ultrasound in SLPTC especially catalyzed by dual-site phase-transfer catalyst was rarely reported and understood.

In the present study, the efficient synthesis of benzyl 4-hydroxybenzoate was developed. Benzyl 4-hydroxybenzoate is

* Corresponding author. Tel.: +886 4 22840510x609; fax: +886 4 22854734.

E-mail address: hmyang@dragon.nchu.edu.tw (H.-M. Yang).

a chemically stable, insoluble in water, low melting point and low price compound and is used as colorless dye, color developing agent, intermediate of liquid crystal and is also widely applied in cosmetics industry [17]. In the past, the substituted hydroxybenzoates are commonly produced from esterification of hydroxybenzoic acid and alcohols in the presence of sulfuric acid, but having disadvantages of severe reaction conditions, low yields, hydrolysis side reactions and special consideration in reactor materials due to sulfuric acid [17,18]. Those drawbacks can be overcome by phase-transfer catalysis and the reaction rate can be enhanced by PTC accompanying with ultrasonic irradiation. The purpose of this work is to investigate esterification process of sodium 4-hydroxybenzoate and benzyl bromide by novel dual-site phase-transfer catalyst BTBAMBC in SLPTC under ultrasonic irradiation (termed as U-SLPTC). The reaction mechanism was also verified by analyzing the variation of the catalytic intermediate in this U-SLPTC system.

2. Experimental

The reagents 4,4'-bis(chloromethyl)-1,1'-biphenyl (95%, from Aldrich, USA), tributylamine (99%, from ACROS, Belgium), benzyl bromide (99%, from Alfa Aesar, USA, denoted as RBr), and 4-hydroxybenzoic acid sodium salt (98%, from Aldrich, USA, denoted as ArCOONa) and phase-transfer catalysts (PTCs) tetra-n-butylphosphonium bromide (99%, from Alfa, USA, denoted as TBPB), tetra-n-butylammonium bromide (99%, from Alfa, USA, denoted as TBAB) and benzyltributylammonium bromide (98%, from ACROS, USA, denoted as BTBAB) were used without further treatments. Other reagents are all reagent-grade chemicals from Lancaster, SHOWA, ACROS, TEDIA, Mallinckvoldt, J.T. Baker, Fluka, ECHO and TCI. The ultrasonic generator was a thermostatic bath equipped with dual frequencies (28/50 kHz or 40/80 kHz) and variable electric powers (max. 300 W with 0.0126 W/cm³ of power density).

2.1. Synthesis of dual-site phase-transfer catalyst BTBAMBC

The dual-site phase-transfer catalyst BTBAMBC was synthesized as follows. A definite amount 0.005 mol of 4,4'-bis(chloromethyl)-1,1'-biphenyl was completely dissolved in 10 cm³ of acetonitrile to react with 0.1 mol of tributylamine at 70 °C and 150 rpm for 24 h. After completing the reaction, acetonitrile solvent was removed to get light yellow raw catalyst for purification. The raw catalyst was first dissolved in 10 cm³ of n-propanol at 70 °C. A quantity 50 cm³ of methyl tert-butyl ether was then introduced very slowly under ultrasonic irradiation for at least 1 h to precipitate white solid catalyst. The solvent was removed by centrifugation. The re-precipitation step was repeated for at least three times and the final solid catalyst was rinsed with n-hexane, followed by drying at 80 °C for 1 h to obtain BTBAMBC.

2.2. Synthesis of the product benzyl 4-hydroxybenzoate

The product benzyl 4-hydroxybenzoate (ArCOOR) was synthesized as follows. An amount 0.013 mol of ArCOONa and 0.0065 mol of TBPB were first dissolved in 40 cm³ of water. Then 0.01 mol of benzyl bromide in 40 cm³ of dichloromethane was added into the above aqueous solution to react at 35 °C and 350 rpm for 24 h. After completing the reaction, the organic phase was separated and rinsed with de-ionized water several times to remove the catalyst, and then concentrated under vacuum to get crude product, which was further purified by column chromatography in the condition of eluent at the ratio of ethyl acetate to n-hexane equal to 1:5. After separating the solvent and drying

under vacuum, the final white solid product was obtained for identification.

2.3. Synthesis of catalytic intermediate and determination of Q²⁺

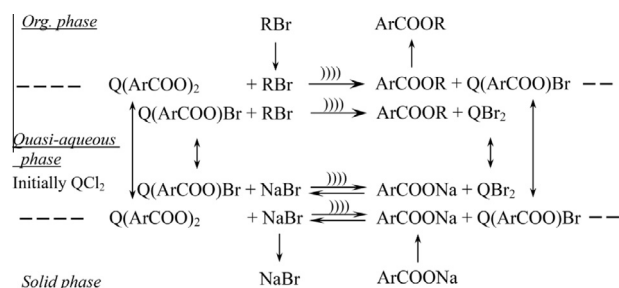
To synthesize the catalytic intermediate Q(ArCOO)₂, 0.001 mol of BTBAMBC and 0.02 mol of ArCOONa were co-dissolved in 40 cm³ of de-ionized water, and reacted at 60 °C and 250 rpm for at least 1 h. The intermediate Q(ArCOO)₂ was precipitated, separated by filtration and washed with water and acetone to eliminate un-reacted residues for at least three times. The purified Q(ArCOO)₂ was identified with NMR. To determine the content of Q(ArCOO)₂ in the third phase, the third phase was first separated and added into methanol containing pre-dissolved diphenyl methane (used as internal standard). A volume 0.2 cm³ of the methanol solution was sampled and further diluted in 4 cm³ of methanol for HPLC analysis. To determine Q²⁺ in the organic phase or the third phase before and after reaction, titration method was applied by using sodium tetraphenyl borate (0.05 N of Na⁺TBP⁻) and bromophenol blue (0.2% in ethanol) as titrant and indicator in water/dichloromethane system. When the end point was reached, the color of dichloromethane phase would change from blue to colorless.

2.4. Ultrasound-assisted solid–liquid phase-transfer catalyzed esterification

The kinetic measurement of the esterification in solid–liquid system was carried out in a thermo-stated batch reactor equipped with ultrasonic generator for each reaction condition. Definite quantities of BTBAMBC (or other PTCs), RBr and diphenyl methane (internal standard) were dissolved in organic solvent and stirred for 15 min in a batch reactor installed in the ultrasonic bath, and reaction temperature was controlled at the desired value. To start the reaction, a definite amount of ArCOONa was introduced into the reactor and the ultrasonic irradiation was activated. At each chosen time, 0.2 cm³ of the organic phase was sampled and diluted in 4 cm³ of methanol for HPLC analysis using C18 column and UV detector at 254 nm with eluent of acetonitrile/methanol/water at 1.0 cm³/min and 37/37/26 (v/v/v).

2.5. Reaction mechanism and kinetic equation

In this solid–liquid reaction system, a thin-layer phase termed as “quasi-aqueous phase” can be formed by adding small amount of water, and is locating between the solid phase and organic phase. In this quasi-aqueous phase, the dissolved reactant salt ArCOONa and catalyst BTBAMBC would react to produce Q(ArCOO)Cl and Q(ArCOO)₂. The organic reactant RBr would transfer from the bulk organic phase to the organic/quasi-aqueous interface to conduct the intrinsic reaction with Q(ArCOO)₂. The reaction mechanism is shown as follows.



Download English Version:

<https://daneshyari.com/en/article/10566128>

Download Persian Version:

<https://daneshyari.com/article/10566128>

[Daneshyari.com](https://daneshyari.com)