Ultrasonics Sonochemistry 21 (2014) 395-400

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

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, solid–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 dualsite 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).

^{1350-4177/\$ -} see front matter @ 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.ultsonch.2013.08.004

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 phasetransfer 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) tetran-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, Mallinckvodt, 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 Q^{2+}

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 cm^3 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).

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(Ar-COO)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.



After the formation of the catalytic intermediate Q(ArCOO)Br and $Q(ArCOO)_2$ in the quasi-aqueous phase, the intrinsic reactions are mainly conducted at the region between the quasi-aqueous and organic phases:

$$RBr_{(org)} + Q(ArCOO)_{2(q-aq)} \xrightarrow{k_1} ArCOOR_{(org)} + Q(ArCOO)Br_{(q-aq)}, \quad (1)$$

$$RBr_{(org)} + Q(ArCOO)Br_{(q-aq)} \xrightarrow{k_2} ArCOOR_{(org)} + QBr_{2(q-aq)}.$$
 (2)

Thus, the rate of formation of ArCOOR in the organic phase is expressed as

$$\frac{d\mathsf{C}_{\mathsf{ArCOOR}}^{\mathsf{org}}}{dt} = (k_1\epsilon_1\mathsf{C}_{\mathsf{Q}(\mathsf{ArCOOR})_2}^{\mathsf{q}-\mathsf{aq}} + k_2\epsilon_2\mathsf{C}_{\mathsf{Q}(\mathsf{ArCOOR})_{\mathsf{Br}}}^{\mathsf{q}-\mathsf{aq}})\mathsf{C}_{\mathsf{RBr}}^{\mathsf{org}},\tag{3}$$

where k_1 and k_2 are reaction rate constants of reactions (1) and (2), and ε_1 and ε_2 are enhancement factors for reactions with ultrasound irradiation. From the experimental results, the content of Q(ArCOO)Br in the quasi-aqueous phase is much less than Q(ArCOO)₂ and is not observable, Eq. (1) can be reduced to

$$\frac{d\mathbf{C}_{\text{ArCOOR}}^{\text{org}}}{dt} = (k_1\epsilon_1 + k_2\epsilon_2\lambda)\mathbf{C}_{\mathbf{Q}(\text{ArCOOR})_2}^{\mathbf{q}-\mathbf{aq}}\mathbf{C}_{\text{RBr}}^{\text{org}},\tag{4}$$

where λ is the molar ratio of Q(ArCOO)Br to Q(ArCOO)₂.Taking molar balance for ArCOONa and neglecting the trace amounts of Q(ACOO)Br and Q(ArCOO)₂ in the organic phase, we have

$$\begin{split} N_{ArCOONa,0} &= N_{ArCOONa}^{S} + N_{ArCOONa}^{q-aq} + V^{q-aq}(2+\lambda) C_{Q(ArCOO)_{2}}^{q-aq} \\ &+ V^{org} C_{(ArCOOR)}^{org}, \end{split}$$
(5)

where V^{q-aq} is the volume of quasi-aqueous phase. $N_{ArCOONa}^{S}$ and $N_{ArCOONa}^{q-aq}$ are the reactant in solid form and the dissolved in the quasisi-aqueous phase with the distribution $N_{ArCOONa}^{S} = \alpha N_{ArCOONa}^{q-aq}$, in which $N_{ArCOONa}^{q-aq}$ would be further converted to $Q(ArCOO)_2$ in the quasisi-aqueous phase. Hence, for simplicity, the efficiency factor η is used to relate $N_{ArCOONa}^{q-aq}$ and $N_{(ArCOO)_2}^{q-aq}$ by the equation $N_{(ArCOO)_2}^{q-aq} = \eta N_{ArCOONa}^{q-aq}$. Substituting this equation into Eq. (5) and rearranging it, the expression for $Q(ArCOO)_2$ is,

$$\frac{C_{(ArCOO)_2}^{q-aq}}{N_{ArCOONa,0}} = \frac{1}{((1+\alpha)/\eta + 2 + \lambda)V^{q-aq}} \left(1 - \frac{V^{org}C_{ArCOOR}^{org}}{N_{ArCOONa,0}}\right)$$
(6)

The product yield (*Y*) based on ArCOONa is defined as the molar ratio of produced ArCOOR to initial addition of limiting reactant ArCOONa, $Y = N_{ArCOOR}/N_{ArCOONa,0}$. For largely excessive molar ratio of RBr to ArCOONa (>14), the change of RBr in the organic phase can be neglected. Thus, substitution of Eq. (6) into (4) yields the pseudo-first-order kinetic equation,

$$\frac{dY}{dt} = \frac{(k_1\epsilon_1 + k_2\epsilon_2\lambda)C_{\text{RBr},0}^{\text{org}}}{((1+\alpha)/\eta + 2 + \lambda)V^{q-\text{aq}}}(1-Y) = k_{app}(1-Y)$$

with the apparent rate coefficient k_{app} to be

$$k_{app} = \frac{(k_1 \epsilon_1 + k_2 \epsilon_2 \lambda) C_{RBr,0}^{org}}{((1+\alpha)/\eta + 2 + \lambda) V^{q-aq}}$$
(7)

Eq. (7) is solved to get $-ln(1 - Y) = k_{app}t$ for correlating the experimental data.

3. Results and discussion

3.1. Reaction mechanism of U-SLPTC

In this U-SLPTC system for reacting sodium 4-hydroxybenzoate and benzyl bromide, the quasi-aqueous phase was found to be located between the organic phase and solid phase by adding small amount of water. The intrinsic reaction was mainly conducted in this organic/quasi-aqueous phases. The distributions of catalytic intermediate $Q(ArCOO)_2$ and catalyst cation Q^{2+} in the organic/ quasi-aqueous phases before and after reactions were analyzed to identify the reaction mechanism. The results are shown in Table 1. In silence condition, before reaction 97% of the added catalyst Q²⁺ existing in the quasi-aqueous phase, within which 77.4% of Q²⁺ was in the form of Q(ArCOO)₂, and after 30 min of reaction, only 52% of added Q^{2+} retained in this phase with 1.1% of Q^{2+} as Q(ArCOO)₂. For the case of ultrasonic irradiation, before reaction 67% of the added Q²⁺ was found in the quasi-aqueous phase with 43.7% of Q^{2+} to be Q(ArCOO)₂, and after 30 min of reaction, there was only 50.5% of added Q^{2+} retained in this phase with 1.1% of Q^{2+} as Q(ArCOO)₂. From these results, ultrasonic irradiation was demonstrated to be able to improve the transfer of both Q^{2+} and Q(ArCOO)₂ from the quasi-aqueous phase into organic phase. When the organic reactant benzyl bromide was introduced to start the reaction, the content of Q(ArCOO)₂ in the quasi-aqueous phase quickly decreased to a fraction of 1.1% of the total added O^{2+} . This phenomenon described that the intrinsic reaction of Q(ArCOO)₂ and RBr mainly conducted in this quasi-aqueous phase, locating in the interfacial region of solid/organic phases.

3.2. Effect of water in U-SLPTC catalyzed by BTBAMBC

In solid-liquid system, the addition of small amount of water can be useful in forming the catalytic intermediate for conducting intrinsic reactions. The effect of water on this SLPTC was explored using BTBAMBC under 250 rpm and ultrasonic irradiation (28 kHz/ 300 W). Fig. 1 is the plot of -ln(1 - Y) versus time for different amounts of water added, showing that pseudo-first-order kinetic equation can be successfully used to describe the U-SLPTC system. Table 2 shows the apparent rate constants for the water effect. Without adding water, only 3.7% of product yield was obtained in 30 min of reaction; but merely with 1 cm³ of water in the system, the product yield largely increased to 84.3%. Continuing to increase the quantity of water, the reaction rate was gradually reduced. When the amount of water was added to 15 cm³, the solid-liquid system became a liquid-liquid type, and the product vield greatly decreased to 19.5%, much lower than that in SLPTC. The increase of reaction rate with small amount of water was mainly due to water solubilizing a small part of solid reactant to increase the production of $Q(ArCOO)_2$ in the quasi-aqueous phase, thus enhancing the intrinsic reaction rate. When more water was added, the effective concentration of Q(ArCOO)₂ in the quasiaqueous phase would be decreased and the reaction rate was reduced. This phenomenon can be verified by the analysis of $Q(ArCOO)_2$ in the organic phase and in the quasi-aqueous phase, as shown in Table 1 and Fig. 2a and b.

The variations of $Q(ArCOO)_2$ in the organic phase and in the quasisi-aqueous phase are shown in Fig. 2a and b. It is noted that most of the formed $Q(ArCOO)_2$ mainly stayed in the quasi-aqueous phase. In the absence of water, the reaction rate of solid reactant and BTBAMBC in the organic phase was very slow, resulting in small product yield 3.7% after 30 min of reaction. With only 1 cm³ of water, the formation of $Q(ArCOO)_2$ greatly increased and concentrated in the quasi-aqueous phase. As shown in Fig. 2b, the molar fraction of $Q(ArCOO)_2$ in the quasi-aqueous phase relative to the total added catalyst Q^{2+} was quickly reduced to about 3.7% in 10 min of reaction, meaning that the intrinsic reaction was fast in the quasi-aqueous phase to get above 65% of product yield.

The interaction of water and catalyst was explored. Four conditions, including case (1) with both water and catalyst, case (2) with water, no catalyst, case (3) with catalyst, no water, and case (4) without water and catalyst, were performed. The results are shown in Fig. 3. For the case (4), only 0.36% of product yield was obtained in 30 min of reaction, and by adding 0.5 mmol of BTBAMBC for case (3), the product yield merely increased to 3.7%. When 1.0 cm³ of

Table 1

Item	Q(ArCOO) _{2,q-aq}	Q(ArCOO) _{2,org}	Q_{q-aq}^{2+}	Q(ArCOO)2,q-aq/ Q_{q-aq}^{2+}	Q(ArCOO)2,q-aq/Q ²⁺ _{total}	$Q_{q-aq}^{2+}/Q_{total}^{2+}$
	(mmol)	(mmol)	(mmol)			
BR#	0.3755	0.0018	0.485	0.774	0.751	0.97
AR [#]	0.0055	0.0059	0.26	0.021	0.011	0.52
BR [*]	0.2183	0.0746	0.335	0.652	0.437	0.67
AR [*]	0.0054	0.0115	0.253	0.021	0.0107	0.51

Conditions: ArCOONa 1 mmol, BTBAMBC 0.5 mmol, RBr 15 mmol, MIBK 15 cm³, water 1 cm³, 250 rpm, 60 °C, reaction time 30 min. AR: after reaction; BR: before reaction; subscript q-aq: quasi-aqueous phase.

Without ultrasound.

With ultrasound (28 kHz/300 W).



Fig. 1. Plot of -ln(1 - Y) versus time for different amounts of water added; 1 mmol of ArCOONa, 15 mmol of RBr, 0.5 mmol of BTBAMBC, 15 cm³ of MIBK, 60 °C, 250 rpm, ultrasound (28 kHz/300 W); water (cm³): (♦) 0, (●) 0.5, (■) 1, (▲) 3, (□) 5, (△) 15.

Table 2

Apparent reaction rate for different amounts of water and PTC.

PTC	Amounts of water	$k_{app} imes 10^2 \ (min^{-1})$	Yield of ArCOOR (%) at reaction time	
	(cm ³)		15 min	30 min
BTBAMBC	0	0.16	3.17	3.70
	0.5	7.31	70.6	73.1
	1.0	10.57	78.9	84.3
	3.0	4.86	46.5	78.3
	5.0	1.18	13.6	32.9
	15.0	0.72	9.92	19.5
TBPB	1.0	8.89	70.6	78.2
BTBAB	1.0	7.89	70.3	81.1
TBAB	1.0	6.81	67.4	77.8

Conditions: ArCOONa 1 mmol, PTC 0.5 mmol, RBr 15 mmol, MIBK 15 cm³, 250 rpm, 60 °C, ultrasound 28 kHz/300 W.

water was employed for case (2), the product yield would increase to 12.0%; by using 1.0 cm³ of water and 0.5 mmol of BTBAMBC, the product yield greatly raised to 84.3%. The reaction system followed the pseudo-first-order kinetics, except for the slight variation in the late reaction period (>20 min) for faster reaction rate that would generate much side product NaBr deposited on the surface of solid reactant to retard the formation of Q(ArCOO)₂ and quickly terminate the reaction. The results strongly reveal that the small amount of water can efficiently promote the solubilization of the solid reactant and thus enhance the formation of catalytic intermediate Q(ArCOO)₂.

3.3. Activities of BTBAMBC and single-site phase-transfer catalysts

To compare the catalytic activity of the prepared BTBAMBC with single-site catalysts in U-SLPTC system, the experiments using 1 cm^3 of water and ultrasound (28 kHz/300 W) were performed, as shown in Table 2. From the product yield in 15 and 30 min of reac-



Fig. 2. Effect of water on the variation of Q(ArCOO)₂ in different phases; conditions the same as that in Fig. 1; water (cm³): (a) in organic phase, (\blacklozenge) 0, (\blacksquare) 1, (\triangle) 15; (b) in quasi-aqueous phase, (♦) 1, (■) 3.



Fig. 3. Effects of water on the reaction rate; 1 mmol of ArCOONa, 15 mmol of RBr, 15 cm³ of MIBK, 60 °C, 250 rpm, ultrasound (28 kHz/300 W); condition: (**A**) 1 cm³ of water, 0.5 mmol of BTBAMBC, (\blacklozenge) no water, 0.5 mmol of BTBAMBC, (\blacklozenge) 1 cm³ of water, no PTC, (■) no PTC, no water.

tion, BTBAMBC exhibited the best catalytic activity than TBPB, TBAB and BTBAB. The order of reaction rate was BTBAMBC > TBPB > BT-BAB > TBPB, and the apparent rate coefficient of BTBAMBC was almost 1.5 times of that of TBAB.

Fig. 4 shows the effect of amounts of BTBAMBC for water at 1.0 cm³ under ultrasonic irradiation (28 kHz/300 W). Without



Fig. 4. Product yield for different amounts of catalyst; 1 mmol of ArCOONa, 15 mmol of RBr, 1 cm^3 of water, 15 cm^3 of MIBK, 60 °C, 250 rpm, ultrasound (28 kHz/300 W); BTBAMBC (mmol): (\blacklozenge) 0, (\blacksquare) 0.1, (\blacklozenge) 0.5, (\Box) 0.7, (\triangle) 1.

using BTBAMBC, it still gave 12.0% of the product yield. The apparent rate coefficients for different amounts of BTBAMBC were 0.045 min⁻¹ (0 mol), 0.143 min⁻¹ (0.1 mol), 1.057 min⁻¹ (0.5 mol), 0.808 min⁻¹ (0.7 mol) and 0.693 min⁻¹ (1.0 mol), respectively. As seen in Eq. (7), the factors that affected apparent rate coefficient by BTBAMBC was mainly reflected in the factors α , η , $k\varepsilon$, and the concentration of Q(ArCOO)₂ in the quasi-aqueous phase. The reaction rate increased with increasing the usage of BTBAMBC, up to 0.5 mol, then decreased even increasing the catalyst amount. It revealed that more catalyst resulted in much faster initial reaction rate, leading to more inorganic salt produced and deposited on the particle surface, hence reducing the contact of the catalyst and the solid reactant, and the reaction rate was quickly diminished and terminated in the late reaction period (>20 min) with slight deviation to pseudo-first-order kinetics.

The polarity of organic solvent affects the dissolution of solid reactant anion in organic solvent. With adding 1 cm^3 of water, the more polar solvent induced the higher activity of phase-transfer catalyst, because a higher content of Q(ArCOO)₂ was acquired. As shown in Table 3, the order of product yield in 30 min of reaction for the tested solvents is MIBK (84.3%) > toluene (16.7%), and n-heptane (3.2%).

3.4. Effects of stirring and ultrasound irradiation

The comparison for the effect of agitation and ultrasound was performed. For applying agitation alone, the apparent rate coefficients for different stirring speeds were 0.0669 min⁻¹ (0 rpm), 0.0843 min⁻¹ (150 rpm), 0.1 min⁻¹ (200 rpm), 0.1057 min⁻¹ (250 rpm) and 0.0937 min⁻¹ (300 rpm). The factors influencing the k_{app} were mainly the distribution factor α and the ultrasonic enhancement factor ε . At 250 rpm without ultrasound, the product

 Table 3

 Apparent reaction rate for different organic solvents and temperatures.

Solvent ([#] DC at 25 °C)	Temperature (°C)	$k_{app} imes 10^2$ (min ⁻¹)	Yield of ArCOOR (%)
MIBK (13.11)	40	0.88	21.1
	50	2.75	51.1
	60	10.57	84.3
	40*	0.57	16.6
	50 [*]	1.49	31.5
	60*	5.63	79.5
Toluene (2.4)	60	0.57	16.7
Heptane (1.92)	60	0.09	3.2

Conditions: ArCOONa 1 mmol, BTBAMBC 0.5 mmol, RBr 15 mmol, solvent 15 cm³, water 1 cm³, 250 rpm, 60 °C, ultrasound 28 kHz/300 W, reaction time 30 min. [#] DC: dielectric constant.

* Without ultrasound.

yield was 79.5% in 30 min of reaction. By applying ultrasound (28 kHz/300 W) and at 250 rpm of stirring, 84.3% of product yield was achieved. This implies that the synergetic effect of ultrasound and stirring enhanced the intrinsic reaction occurring in the quasi-aqueous phase (Fig. 5).

For temperature effect, at 55 °C, the yield was only 58.4% in 30 min, while at 60 °C, the yield raised to 78.9% only in 15 min of reaction, showing significant increase in reaction rate by temperature rise. The apparent rate coefficients using MIBK solvent are shown in Table 3. The Arrhenius' equation $k_{app} = Aexp(-E_{app}/RT)$ was used to correlate the experimental data. The apparent activation energy was obtained to be 24.05 kcal/mol, and $k_{app} = 4.85 \times 10^{14} exp(-24050/RT)$. This high activation energy demonstrates that this U-SLPTC with dual-site phase-transfer catalvst BTBAMBC was reaction-controlled and the mass-transfer resistance between phases was unimportant under ultrasonic irradiation. Fig. 6 shows the profiles of $O(ArCOO)_2$ in the organic phase for different temperatures. Although the main reaction was conducted in the guasi-aqueous phase, but the content of Q(ArCOO)₂ in the organic phase would be increased during the progress of reaction, and more catalytic intermediate was transferred into the organic phase.

Ultrasonic frequency affects the surface morphology of the particulate phase from the impact of liquid-jet and hot-spot generated by ultrasonic waves, that in turn influences the reaction rate, as shown in Eq. (7). The results are depicted in Fig. 7a and b. The order of apparent rate coefficient for tested frequency (k_{app} , kHz) was (0.1057 min⁻¹, 28 kHz) > (0.0742 min⁻¹, 40 kHz) > (0.0635 min⁻¹, 80 kHz) > (0.0563 min⁻¹, 0 kHz). The higher ultrasonic frequency induced less powerful liquid-jet due to the shorter time for bubble growth. The defect occurred on the solid surface was relatively



Fig. 5. Effects of ultrasound and stirring on the reaction; 1 mmol of ArCOONa, 15 mmol of RBr, 0.5 mmol of BTBAMBC, 15 cm³ of MIBK, 1 cm³ of water, 60 °C; condition: (\blacklozenge) ultrasound (28 kHz/300 W), (\blacksquare) stirring (250 rpm), (\blacktriangle) ultrasound (28 kHz/300 W) and stirring (250 rpm).



Fig. 6. Temperature effect for Q(ArCOO)₂ in the organic phase; 1 mmol of ArCOONa, 15 mmol of RBr, 0.5 mmol of BTBAMBC, 1 cm³ of water, 15 cm³ of MIBK, 60 °C, 250 rpm, ultrasound (28 kHz/300 W); temperature (°C): (\diamond) 45, (\Box) 50, (\bigcirc) 60, (\triangle) 65.



Fig. 7. Effect of ultrasonic frequency (a) on the product yield, (b) on the variation of $Q(ArCOO)_2$ in the organic phase; 1 mmol of ArCOONa, 15 mmol of RBr, 0.5 mmol of BTBAMBC, 1 cm³ of water, 15 cm³ of MIBK, 60 °C, 250 rpm, 300 W of ultrasonic power; ultrasonic frequency (kHz): (\bigcirc) 0, (\diamond) 28, (\square) 40, (\triangle) 80.



Fig. 8. Plot of -ln(1 - Y) versus time for effect of ultrasonic power; 1 mmol of ArCOONa, 15 mmol of RBr, 0.5 mmol of BTBAMBC, 1 cm³ of water, 15 cm³ of MIBK, 60 °C, 250 rpm, 28 kHz of ultrasonic frequency; ultrasonic power (W): (\bigcirc) 0, (\diamond) 100, (\square) 200, (\triangle) 300.

small and the deposited inorganic salts would be less sheared, leading to slower formation of $Q(ArCOO)_2$ (Fig. 7b).

The effect of electric power of ultrasound was evaluated for 0, 100, 200 and 300 W, as shown in Fig. 8. From the pseudo-first-order plots, the apparent rate coefficients were found to be 0.0563 min⁻¹ for 0 W, 0.0759 min⁻¹ for 100 W, 0.092 min⁻¹ for 200 W and 0.1057 min⁻¹ for 300 W, respectively. With no doubt, the reaction rate increased with increasing ultrasonic power, showing the 88% increase of reaction rate by 28 kHz/300 W of ultrasonic irradiation.

4. Conclusion

In the present study, the novel dual-site phase-transfer catalyst BTBAMBC was synthesized and used to catalyze esterification of sodium 4-hydroxybenzoate and benzyl bromide under ultrasonic irradiation in solid–liquid system. The quasi-aqueous phase was generated by adding water and the prepared catalyst. Ultrasound can effectively enhance the overall reaction and the surface deposited side-product can be removed by liquid-jet generated from ultrasonic waves. The reaction mechanism of U-SLPTC was identified by analyzing the variation and distribution of the catalytic intermediate between phases. The esterification catalyzed by BTBAMBC using U-SLPTC was developed.

Acknowledgments

The authors acknowledge the financial support of the National Science Council, Taiwan, ROC (Grant No. NSC 99-2221-E-005-092). This work is also supported in part by the Ministry of Education, Taiwan, ROC, under the ATU plan.

References

- C.M. Starks, C.L. Liotta, M. Halpern, Phase-Transfer Catalysis: Fundamental, Applications and Industrial Perspectives, Chapman & Hall, New York, 1994.
- [2] H.M. Yang, H.S. Wu, Interfacial mechanism and kinetics of phase-transfer catalysis, Catal. Rev. -Sci. Eng. 45 (2003) 463-540.
- [3] N. Ge, Y. Zhang, D. Shi, Q. Gu, X. Zhu, Z. Ding, Novelties of solid-liquid phase transfer catalyzed synthesis of benzyl diethyl phosphate from the sodium salt of diethyl phosphate, Eur. J. Chem. 2 (2011) 269–271.
- [4] S. Baj, A. Chrobak, I. Gottwald, Application of solid-liquid phase transfer catalysis system for peroxyester synthesis: a kinetic study of hydroperoxides acylation in the presence of solid sodium carbonate, Appl. Catal., A 224 (2002) 89–95.
- [5] H.M. Yang, C.M. Wu, Phase-transfer catalyzed allylation of sodium phenoxide in solid–liquid system, J. Mol. Catal. A: Chem. 153 (2010) 83–91.
- [6] H.M. Yang, P.I. Wu, Kinetics of phase-transfer catalyzed esterification of aliphatic dicarboxylate in solid-liquid system, Appl. Catal., A 209 (2001) 17-26.
- [7] H.M. Yang, C.M. Wu, H.E. Wu, Kinetics for phenolysis of ethyl 2-bromoisobutyrate via phase-transfer catalysis in a solid–liquid system, J. Chem. Technol. Biotechnol. 75 (2000) 387–393.
- [8] H.M. Yang, P.I. Wu, C.M. Li, Etherification of halo-eater by phase-transfer catalysis in solid-liquid system, Appl. Catal., A 193 (2000) 129–137.
- [9] H.E.-S. Ali, Cycloalkylation reactions of fatty amines with a, x-dihaloalkanes: role of bis-quaternary ammonium salts as phase-transfer catalysts, Catal. Commun. 8 (2007) 855–860.
- [10] J.L. Luche, Synthetic Organic Sonochemistry, Plenum Press, NewYork, 1998.
- [11] M.L. Wang, V. Rajendran, Ultrasound assisted phase-transfer catalytic epoxidation of 1,7-octadiene – a kinetic study, Ultrason. Sonochem. 14 (2007) 46–54.
- [12] J.T. Li, X.L. Li, An efficient and practical synthesis of methylene dioximes by combination of ultrasound and phase transfer catalyst, Ultrason. Sonochem. 14 (2007) 677–679.
- [13] H. Xu, Y. Chen, An efficient and practical synthesis of mandelic acid by combination of complex phase transfer catalyst and ultrasonic irradiation, Ultrason. Sonochem. 15 (2008) 930–932.
- [14] H.M. Yang, G.Y. Peng, Ultrasound-assisted third-liquid phase-transfer catalyzed esterification of sodium salicylate in a continuous two-phase flow reactor, Ultrason. Sonochem. 17 (2010) 239–245.
- [15] H.M. Yang, C.C. Chiu, Ultrasound-assisted phase-transfer catalysis: benzoylation of sodium 4-acetylphenoxide by dual-site phase-transfer catalyst in a tri-liquid system, Ultrason. Sonochem. 18 (2011) 363–369.
- [16] H.M. Yang, Y.C. Chen, Ultrasound-assisted third-liquid phase-transfer catalyzed esterification of potassium 4-methoxyphenylacetate by dual-site phase-transfer catalyst, J. Taiwan Inst. Chem. Eng. 43 (2012) 897–903.
- [17] Y. Hu, X. Liu, L. Wang, Study on synthesis of benzyl p-hydroxybenzoate by phase transfer catalysis, Huaxue Shiji 26 (2004) 363–365.
- [18] D. Peng, G. Xiong, W. Xu, New method for synthesis of benzyl p-hydroxybenzoate, Shipin Gongye Keji 25 (2004) 113–115.