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Research Article

Ultrasonically Promoted Synthesis of Ethyl 2-(naphthalen-2-yloxy)acetate in Solid-Liquid Heterogeneous Phase Transfer Catalysis Condition

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Abstract

In this paper, the synthesis of ethyl 2-(naphthalen-2-yloxy)acetate from *β*-naphthol and ethyl 2-bromoacetate under ultrasound and catalyzed by quaternary ammonium salt in solid-liquid heterogeneous condition was described. Trace amount of water play a major role in this solid-liquid reaction. The reaction follows pseudo first order rate law. The apparent rate constant of the organic phase reaction was obtained form the experimental data. The combination of small amount of tetrabutylammonium bromide (TBAB) and ultrasound (k_{app} = 25.22×10^{-3} min^{-1}) shows several fold enhanced rate of the reaction than the conventional operation (k_{app} = 6.42×10^{-3} min^{-1} for TBAB only). The rate constant increases (0.05 to 0.3 g) with increase in the concentration of catalyst (from k_{app} = 10.12×10^{-3} min^{-1} to k_{app} = 34.46×10^{-3} min^{-1}). The other kinetic effects such as, effect of agitation speed, kind of frequency of ultrasound, kind of various quantity of K_2CO_3, quantity of water, temperature, different quaternary ammonium salts, solvents and volume of organic solvents on the conversion of ethyl 2-bromoacetate and apparent rate constant were investigated in detail and rational explanations are provided.

Keywords: phase-transfer catalyst; solid-liquid mode; ethyl 2-bromoacetate; ethyl 2-(naphthalen-2-yloxy)acetate; ultrasonication

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1. Introduction

Phase-transfer catalysis (PTC) [1-3] is an effective technique for conducting heterogeneous reactions where the reagents are located in different phases [4]. In order to reaction take place, the pinch of phase-transfer catalyst was added to the reaction system. The phase-transfer agent must forming active catalyst with the reactant anion from the aqueous or solid phase and transports it through the interfacial region into the organic phase [5] for an ion-pair extraction of normal phase-transfer catalysis. Undoubtedly, PTC offers many substantial advantages for the practical execution of numerous reactions [6]. PTC technology is now used in the manufacture of an extremely wide variety of chemicals such as polymers, petrochemicals, pharmaceuticals, agrochemicals and other commodities, specialty and fine

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chemicals. According to reaction medium, the heterogeneous phase-transfer catalysis reactions are mainly classified into two categories as solid-liquid PTC (SL-PTC) and liquid-liquid PTC (LL-PTC).

Phase-transfer catalysis offers several advantages like high reaction rate, high yield, high selectivity towards desired product, low energy requirement and operates at milder reaction condition [7]. Among the several PTCs are available, quaternary ammonium salts are the one which is frequently used by many researchers. In recent days, the application of ultrasound in organic synthesis has been enhanced the reaction because of shorter reaction time, increased yield and selectivity of product and energy consumption, etc. [8]. Now researchers are more interested to attempt the reaction with the combination of ultrasound and PTC carried in immiscible heterogeneous reaction under mild and environmentally benign methodology to obtain maximum yield or conversion [9-14].

Sonochemistry, the chemistry associated with ultrasound which is governed by parameters like amplitude and frequency of an applied sound field, temperature, surface tension, vapour pressure, gas content and nuclei density of the solution as well as vessel and probe geometry [15]. Applications for sonochemistry can be found in many areas, but sonochemical processes are most widely developed for heterogeneous reactions [16]. There are two types of effects mediated by ultrasound: chemical and physical. A specific effect is the asymmetric collapse near a solid surface, which forms microjets. These effects of ultrasound were very effective in cleaning and also responsible for rate acceleration in multiphasic reactions, since surface cleaning and erosion lead to improved mass transport.

The product is an ether-ester which is very easily hydrolyzed in alkaline solutions [17]. By applying the SL-PTC, this hydrolysis side reaction can be prevented. The ethyl 2-(naphthalen-2-yloxy)acetate was the starting material which is transformed to several products with different reactants, in which most of products have antimicrobial activity [18-20].

The main objective of this work is to provide the simple and efficient way to synthesize the ethyl 2-(naphthalen-2-yloxy)acetate which is synthetically useful compound under environmentally benign methods like ultrasound and PTC, in solid-liquid heterogeneous condition. The kinetic aspects on the synthesis of ethyl 2-(naphthalen-2-yloxy)acetate such as the effects of agitation speed, kind of frequency of ultrasound, kind of various quantity of K_2CO_3, quantity of water, temperature, quantity of TBAB, quaternary ammonium salts, solvents and volume of organic solvents were well studied in detail and proposed suitable mechanism for this reaction.

2. Experimental

2.1. Catalysts, chemicals and solvents

All the reagents, including, β-naphthol (Merck, 98%), ethyl 2-bromoactate (Avra synthesis Pvt Lt, Hyderabad, India. 97%), biphenyl (Merck, 99%), tetra-n-butylammonium iodide (TBAI), tetra-n-butylammonium bromide (TBAB), tetra-n-butylammonium hydrogen sulfate (TBAHS), tetra-n-butylphosphonium bromide (TBPB) and tetra-n-butylammonium chloride (TBAC) were obtained from Avra, Merck, SD Fine chemicals. Potassium carbonate, toluene, chlorobenzene, chloroform, o-dichlorobenzene, n-hexane and other reagents for synthesis were guaranteed grade (GR) chemicals and were used without further purification.

2.2. Instrumentation

^{1}H NMR was recorded on a Bruker 300 MHz and ^{13}C spectra were recorded on 75 MHz respectively using TMS as an internal standard. Gas chromatography was carried out using a GC-Varian 3700 model. Ultrasonic water bath was obtained from Equitron, Media Instrument Manufacturing Company, Chennai, India-600 004.

2.3. Ultrasonic process equipment

Ultrasonic energy is transmitted to the process vessel through the liquid medium, usually water in the tank. For safety purpose, the sonochemical reactor consisted of two layers stainless steel body. The sonochemical reactor configuration used in the present work is basically an ultrasonic bath. The internal dimension of the ultrasonic cleaner tank is 48×28×20 cm with liquid holding capacity of 5 liters. Two types of frequencies of ultrasound were used in these experiments, which are 28 kHz and 40 kHz with each output as 300 W. Both ultrasounds separately produces through a flat transducer mounted at the bottom of the sonicator. The reactor was a 250 mL three-necked Pyrex round-bottom flask. This reaction vessel was supported at the centre of the ultrasonic cleaning bath 2 cm above from the position of the transducer to get the maximum ultrasound energy. All the experimental parameters were done at 40 kHz with output power of 300 W.

2.4. Kinetics of synthesis of ethyl 2-(naphthalen-2-yloxy)acetate

The reaction was conducted on a 250 mL three-necked Pyrex round-bottom flask this permits agitating the solution, inserting the water condenser to recover organic reactant and taking samples and feeding the reactants. This reaction vessel was supported at the centre of the sonicator. Known quantities of chlorobenzene (30 mL), dried potassium carbonate (2.5 g in 0.5 mL water) and 0.2 g biphenyl (IS-internal standard) were introduced into the reactor. Then, 6 g of β-naphthol and 1 g of ethyl 2-bromoacetate, 0.2 g of TBAB were introduced to the reactor to start the reaction. The reaction mixture was stirred at 600 rpm. The phase separation was almost immediate on arresting the stirring process. Samples were collected from the organic layer at regular time intervals and 0.5 mL of chlorobenzene was added to vials to dilute the solution. The kinetics was followed by estimating the amount of ethyl 2-bromoacetate (limiting reagent) that disappeared and measured by a gas Chromatography (GC-Varian 3700 model). The analyzing conditions were as follows: Column, 30 m × 0.525 mm i.d. capillary column containing 100% poly(dimethyl siloxanen); injection temperature, 250 ^{o}C; FID detector (300 ^{o}C). Yields were determined from standard curve using biphenyl as an internal standard.

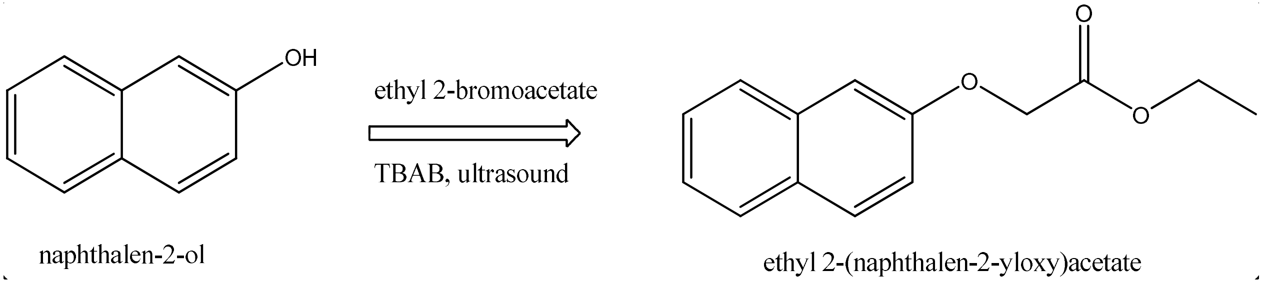
2.5. Spectral data of ethyl 2-(naphthalen-2-yloxy)acetate

After reaction completed, the organic phase solution was concentrated in a vacuum evaporator. Then the remaining organic solution and 30 mL dichloromethane was poured into the extractor (separating funnel). The organic solution is extracted five times with deionized water to remove excess aqueous reactant, catalyst and base. The organic solution further concentrated by vacuum evaporator to obtain the colorless liquid. The obtained compound was characterized by NMR techniques (Scheme 1):

^{1}H NMR (300 MHz, $CDCl_3$): δ. 1.255-1.301 (3H, t, $-CH_3$), 4.208-4.277 (2H, q, $-O-CH_2-CH_3$), 4.574 (2H, s, $-O-CH_2-C=O$), 7.053-7.134 (2H, m, Ar–H), 7.249-7.282 (1H, t, Ar–H), 7.354-7.392 (1H, q, Ar–H), 7.639-7.700 (3H, m, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$): Aliphatic carbons: δ 14.06 ($-CH_3$), 60.51 ($-O-CH_2-CH_3$), 67.80 ($-CH_2$ Carbon in between ether and keto gruop), 168.64 (Ketone Carbon). Aromatic carbons: δ 106.72, 119.21, 123.61, 126.43, 126.88, 127.81, 129.10, 129.46, 134.87, 157.34, Ketone carbon: δ 168.08.

3. Reaction Mechanism and Kinetic Model

The solid-liquid reaction mechanisms are classified into two categories. First one is the non-soluble system (heterogeneous solubilization) introduced by Doraiswamy and Naik [21] and other is soluble system (homogeneous solubilization) introduced by Yadav and Sharma [22]. In this work, β-naphthol dissolved in the organic solvent with the addition of quaternary ammonium salt (QBr). First, deprotanation of ArOH occurs in the interface by the K_2CO_3 produces the potassium salt of β-naphthol (ArO^-K^+) and second, anion exchange reaction with QBr giving the inorganic salt KBr and active intermediate ArOQ in the interface. Then active intermediate is transported to the organic phase and KBr is precipitated as solid. In a similar way, Vander Zwan and Hartner [23] and Sasson and Zahalka [24] proved that quaternary ammonium salt can be used to dissolve the solid reactant. Third, the "active intermediate" ArOQ (org) then react with ethyl 2-bromoacetate (EBA) to produce the desired product (Scheme 2) and the catalyst is



Scheme 1. Synthesis of ethyl 2-(naphthalen-2-yloxy)acetate

regenerated and the above said cyclic process take place continuously up to the disappearance of ethyl 2-bromoacetate in the bulk organic phase.

3.1. Definition

The conversion (X) of ethyl 2-bromoacetate (EBA) is defines in Equation (1):

$$X=1-\{[EBA]_0 / [EBA]_{.o,i}\} \quad (1)$$

where $[EBA]_o$ and $[EBA]_{o,i}$ represent the concentration of ethyl 2-bromoacetate at time (t), t=0 and t>0, respectively.

3.2. Rate expression

The rate expression for this reaction may be expressed in Equation (2):

$$-r_{EBA} = k_{app}\,[EBA]_o \quad (2)$$

where k_{app} is the apparent reaction rate constant.

This reaction is carried out in a batch reactor, so the diminution rate of EBA with time (t) can be expressed in Equation (3):

$$-d[EBA]_0/dt = -r_{EBA} = k_{app}\,[EBA]_o \quad (3)$$

By integrating Equation (3), we get the following Equation (4):

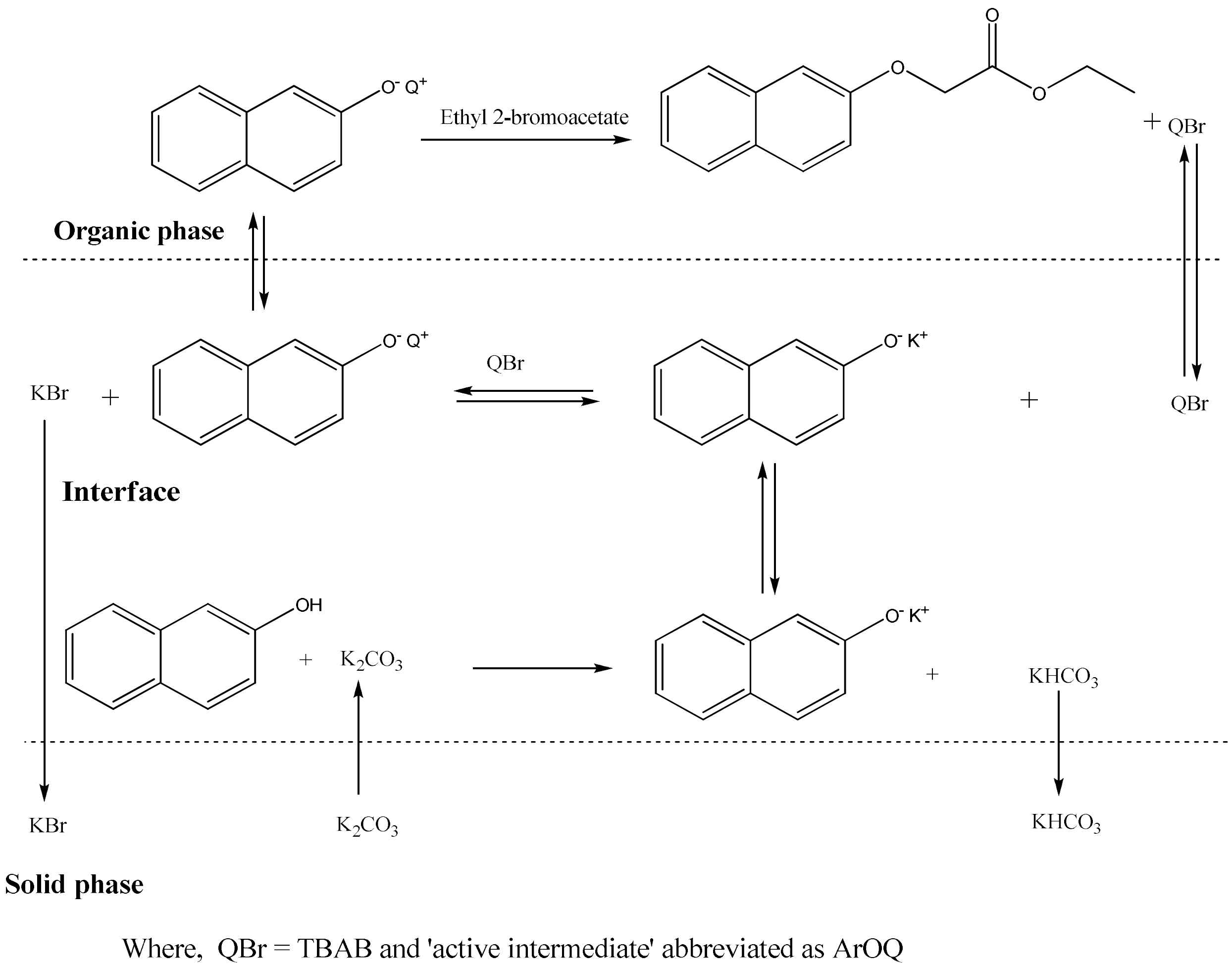
$$-\ln\{[EBA]_0/[EBA]_{.o,i}\} = -\ln(1-X) = k_{app}\,t \quad (4)$$

Using Equation (4), we can get the k_{app} value experimentally by plotting –ln(1-X) against time, (t).

4. Results and Discussion

4.1. Effects of stirring speed

The effect of various stirring speed on the rate of ester-etherification of β-naphthol with ethyl 2-bromoacetate using TBAB as catalyst was studied in the range of 0-800 rpm in the presence of ultrasound energy (40 kHz, 300 W).



Scheme 2. Mechanism for the ester-etherification reaction

From the plots of -ln(1-X) versus time, the pseudo-first order rate constants were evaluated (Figure 1). As shown in Figure 1, there was a significant increase in the apparent rate constant (k_{app}) from 0 to 300 rpm, but it remains constant from 300 to 800 rpm. This phenomenon indicates that the influence of the external mass transfer resistance on the reaction beyond 300 rpm is small. Thus, the organic-phase reaction was obviously a rate-determining step at 300-800 rpm. All subsequent reactions were carried at 600 rpm to assess the effect of various factors on the rate of reaction. The reaction was carried out in ultrasound irradiation without stirring, the k_{app} is to be 2.13×10^{-3} min^{-1}. The same reaction was carried out in the stirring speed of 600 rpm without ultrasound irradiation, the observed kapp value ($k_{app} = 6.42\times10^{-3}$, min^{-1}) was almost 3.9 times lesser than in the presence of both ultrasound irradiation (40 kHz, 300 W) and stirring ($k_{app} = 25.22\times10^{-3}$ min^{-1}).

On the basis of experimental observation, the reaction is still enhanced by ultrasonic irradiation even when the reaction is not agitated by the stirrer. The ultrasonic wave also enhanced the reaction rate due to an increase in the collision rate between the organic-aqueous phase [25]. It is believed that the interfacial area between two phases is affected by both agitation speed and use of ultrasound and which are responsible of the enhancement of the kinetics by harsh mixing, enhancement of mass transfer, especially in solid-liquid systems, high erosion of the solid particles occurs and the surface area is increased [26].

4.2. Effect of ultrasonic frequencies

In our experiments, ultrasonic equipment used was described in the experimental Section. The reaction rates at 28 kHz and 40 kHz were compared with same output power of 300 W. The effect of the ultrasonic frequency on the apparent rate constant (k_{app}) is shown in Table 1. At 90 min, without ultrasonic irradiation the reaction rate (k_{app}) is 6.42×10^{-3} min^{-1}. In the presence of ultrasound frequency 28 kHz, the reaction rate (k_{app}) is 13.51×10^{-3} min^{-1}. In the presence of ultrasound frequency 40 kHz, the reaction rate 25.22×10^{-3} min^{-1}.

From this observed result ultrasonic assisted phase-transfer catalysis significantly improves the reaction rate. The same trend is also observed [27, 28]. In conclusion, the ultrasonic effect enhances the rate several fold with respect to the conventional method (agitation speed at 600 rpm only). Thus, all the experimental parameters were done at 40 kHz with an output power of 300 W.

4.3. Effect of amount of TBAB loading

There was very little reaction in the absence of PTC. The concentration of catalyst (TBAB) was varied from 0.05 to 0.3 g, maintaining all other experimental conditions as constant in the presence of ultrasound (40 kHz, 300 W).

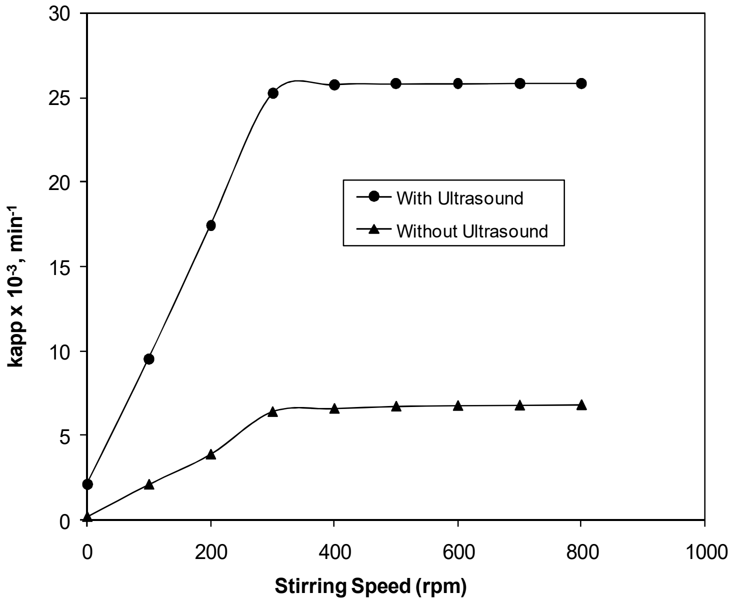


Figure 1. Effect of stirring speed on k_{app}. Condition: 2.5 g of K_2CO_3, 0.5 mL H_2O, 0.2 g of biphenyl (internal standard), 6 g of β-naphthol, 1 g of ethyl 2-bromoacteate, 0.2 g of TBAB, 30 mL of chlorobenzene, 50 ^oC, 40 kHz, 300 W

Figure 2 shows the effect of catalyst loading on the conversion of ethyl 2-bromoacetate. As is typical for all PTC reactions, the conversion or rate of the reaction was found to increase with increasing the catalyst loading. The increase in the conversion or rate of the reaction was mainly attributed to the synergistic effect of ultrasound, i.e. induce the surface area, change the size, and morphology of phase-transfer catalyst [29-31]. Further, the opportunity of collision between active intermediate and reactant present in the organic phase is increased by increasing catalyst concentration. Hence, the apparent rate constant values increased with the increase in the amount of catalyst.

4.4 Effect of the concentration of ethyl 2-bromoacetate

The kinetic experiments were performed by varying the substrate amount ranging from 0.5-1.5 g, maintain the other reactants such as β-naphthol and potassium carbonate in excess. The kapp values are calculated from the plots of -ln(1-*X*) versus time. The data clearly indicates that the k_{app} value increases with increasing the amount of ethyl 2-bromoacetate (EBA). This observation due to presence of PTC and higher concentration of substrate (EBA) had co-operatively influence the reaction and thus enhance the more number of contacts between catalyst and substrate (EBA), and hence it is reflected in enhanced k_{app} values (Table 2). In addition ultrasound enhance the rate of the reaction, it may be due to reduces the surface area between the solid and organic phase, and hence more reactants collide to each other simultaneously we get higher k_{app} value [32].

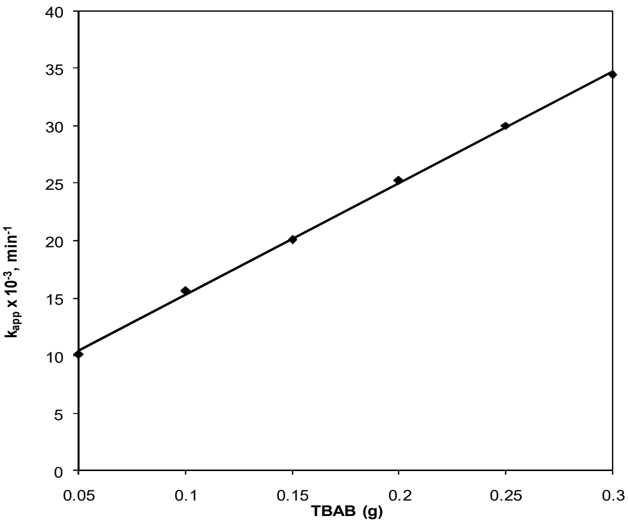


Figure 2. Effect of TBAB amount on k_{app}. Condition: 2.5 g of K_2CO_3, 0.5 mL H_2O, 0.2 g of biphenyl (internal standard), 6 g of β-naphthol, 1 g of ethyl 2-bromoacteate, 600 rpm, 30 mL of chlorobenzene, 50 ^{0}C, 40 kHz, 300 W

4.5. Effect of temperature

The effect of temperature on rate of reaction between β-naphthol and ethyl 2-bromoacetate was studied for the standard conditions. The temperature was varied from 40 to 80 ^{o}C (Figure 3). The conversion of ethyl 2-bromoacetate was observed to increase with increase in reaction temperature along with ultrasonication. This is due to the number of reactant molecules which possess higher activated energy at a higher temperature and thus the ultrasonic wave easily passes through the reactor and increases the collision between the reactants. Generally, the applied ultrasonic frequency induces various degrees of “cavity factor”. The cavity factor otherwise called cavitational effect. It is the propagation of ultrasound through a liquid solution in the reactor induces both physical and chemical processes by acoustic cavitation: the formation, growth and adiabatically implosive collapse of bubbles in the liquid solution. The final collapse of the bubbles produces extremely high temperatures (> 5000 ^{o}C) and pressures (>100 MPa), which accelerated the reaction. The Arrhenius plot was made to determine the energy of activation as 9.99 kcal.mol^{-1} (Figure 6). This value also demonstrates that the reaction is kinetically controlled and an indicative of the interfacial mechanism [33, 34].

4.6. Effect of organic solvents

According to solid-liquid PTC reaction systems, intrinsic reactions including the rate con-

Table 1. Effect of ultrasound frequencies on the reaction rate: 2.5 g of K_2CO_3, in 0.5 mL H_2O, 0.2 g of biphenyl (internal standard), 6 g of β-naphthol, 1 g of ethyl 2-bromoacteate, 0.2 g of TBAB, 30 mL of chlorobenzene, 600 rpm, 50 ^{o}C

Ultrasonic frequencies (kHz)	$k_{app} \times 10^3$, min^{-1}
0	6.42
28	13.51
40	25.22

stants and the rate are highly affected by the organic solvents. Various solvents have different reaction rates. In this work, five organic solvents were applied to investigate the effect of their polarities and dielectric constants (ε) on the S-L PTC and ultrasonication system. As in Table 3, the order of reactivities of these five solvents is: o-dichlorobenzene > chlorobenzene > chloroform > toluene > hexane. It was clearly found that the apparent rate constant increased with the dielectric constant of the solvents but did not increase with the polarity. In order to enhance the apparent rate constant, using a high dielectric constant solvent is favorable for the reaction. In addition, the degradation of any organic solvent was not observed during or after the reaction. The results are also shown in Table 3. It was clearly found that the apparent rate constant increases with the dielectric constant of the solvents but does not increase with the polarity.

4.7. Effect of volume of chlorobenzene

To study the volume of chlorobenzene on the rate of the reaction, the volume was varied from 30-70 mL under sonocatalyzed condition. The conversion or the reaction rate is directly proportional to the concentration of the reactants in organic phase in 90 min of reaction (Table 4). This indicates that a low (diluted) concentration of reactant present in the organic phase, active catalyst ArOQ(org) is decreased with the increase in the volume of chlorobenzene. Hence, the probability of collision between the active catalyst ArOQ(org) and the reactant at larger volume of chlorobenzene was not significant. In order to enhance the apparent rate constant, small volume of chlorobenzene was favorable for the reaction (Table 4).

4.8. Effect of different phase-transfer catalysts

Five different phase-transfer catalysts were employed to explore their efficacy for this reaction. The catalysts tested were tetra-n-butylammonium iodide (TBAI), tetra-n-butylammonium bromide (TBAB), tetra-n-butylammonium hydrogen sulfate (TBAHS), tetra-n-butylphosphonium bromide (TBPB) and tetra-n-butylammonium chloride (TBAC). The results and the corresponding rate constants are shown in Table 5. From Table 5, it is clear that both TBAB and TBPB catalysts show higher activity. The order catalytic reactivity of PTC's are TBPB > TBAB > TBAI approximately equal to TBAHS > TBAC [35, 36]. This indicates that a more lipophilic quaternary cation more easily solvates the solid reactant anion, thus a faster initial reaction rate was obtained. Moreover, the deactivation of TBAI catalyst was greater than that of others. This may be due to larger ionic size of iodide reducing the solubility of ArOQ in chlorobenzene. The production of KI from the reaction of KBr with TBAI may also retard the formation and concentration of ArOQ in the organic phase, thus reducing the reaction rate.

4.9. Effect of various potassium carbonate concentrations

The rate of reaction is tremendously to be affected by a concentration of the alkaline K_2CO_3. The rate of ester-etherification of *β*-naphthol strongly depends on the strength of the potassium carbonate [37]. Kinetic

Table 2. Effect of amount of ethyl 2-bromoacetate (EBA): 2.5 g of K_2CO_3, 0.5 mL H_2O, 0.2 g of biphenyl (internal standard), 6 g of *β*-naphthol, 0.2 g of TBAB, 30 mL of chlorobenzene, 600 rpm, 50 °C, 40 kHz, 300 W

Ethyl 2-bromoacetate (EBA), g	$k_{app} \times 10^3$, min^{-1}
0.5	15.38
0.75	19.621
1	25.22
1.25	29.60
1.5	33.08

Table 3. Influence of organic solvents on the reaction rate: 2.5 g of K_2CO_3, 0.5 mL H_2O, 0.2 g of biphenyl (internal standard), 6 g of *β*-naphthol, 1 g of ethyl 2-bromoacteate,0.2 g of TBAB, 30 mL of solvents, 600 rpm, 50 °C, 40 kHz, 300 W

Solvents	Dielectric constant (ε^a)	$k_{app} \times 10^3$ (min^{-1})
Chlorobenzene	5.6	25.22
O-dichlorobenzene	9.93	28.24
Toluene	2.4	17.12
Hexane	1.89	12.52
Chloroform	4.8	22.13

experiments were carried out by employing 0 to 2.5 g of K_2CO_3 (0.5 mL water constant) under otherwise similar reaction conditions. The conversion or rate of reaction was tremendously increased with increasing in basicity (Figure 4). The main reasons are on increasing the alkaline concentration, the amount of production of anion (ArO^-) is increased and distribution of active catalyst (ArOQ) is increased. From the Figure 4, the conversion is increased linearly increase in the alkali concentration. The water has a subtle influence on the basicity of K_2CO_3 and the hydration of the ion-pair. In order to increase the apparent rate constant (k_{app}), it is favorable for the reaction to use less water or be in an anhydrous condition. Thus, that is the reason why the reaction was carried out in a solid-liquid solution in this work [38, 39].

4.10. Effect of water

In past efforts for solid-liquid phase-transfer-catalyzed systems, additions of water were generally required small quantity or no addition of water is required when quaternary ammonium salts as the catalysts were used. However, in order to investigate the effect of water on the present system, different amounts of water were used and the results are shown in Figure 5. On adding 0-2 mL of water, the

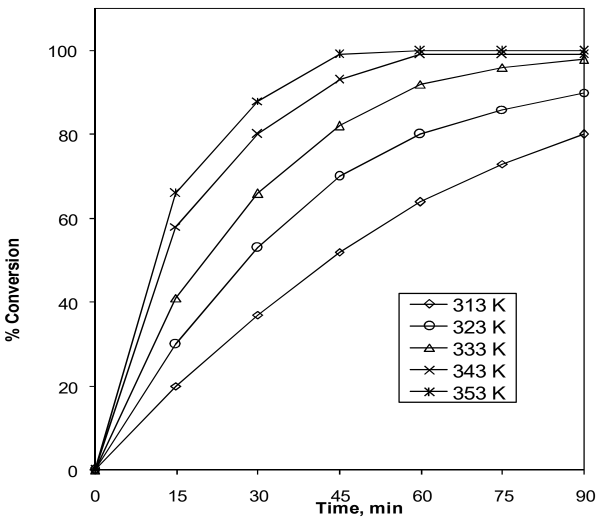


Figure 3. Effect of temperature on conversion. Condition: 2.5 g of K_2CO_3, 0.5 mL H_2O, 0.2 g of biphenyl (internal standard), 6 g of β-naphthol, 1 g of ethyl 2-bromoacteate, 0.2 g of TBAB, 30 mL of chlorobenzene, 600 rpm, 40 kHz, 300 W

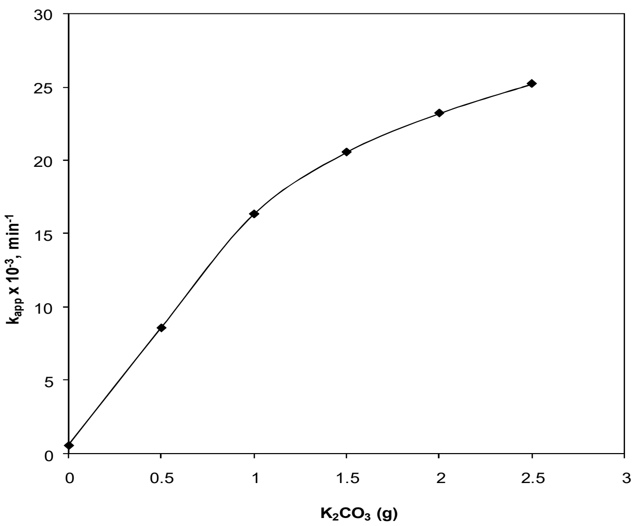


Figure 4. Effect of concentration of potassium carbonate. Condition: 0.5 mL H_2O, 0.2 g of biphenyl (internal standard), 6 g of β-naphthol, 1 g of ethyl 2-bromoacteate, 0.2 g of TBAB, 30 mL of chlorobenzene, 50 ^{0}C, 600 rpm, 40 kHz, 300 W

Table 4. Effect of volume of chlorobenzene on the rate of reaction: 2.5 g of K_2CO_3, 0.5 mL H_2O, 0.2 g of biphenyl (internal standard), 6 g of β-naphthol, 1 g of ethyl 2-bromoacteate, 0.2 g of TBAB, 600 rpm, 50 ^{0}C, 40 kHz, 300 W

Volume of chlorobenzene (mL)	$k_{app} \times 10^3$, min^{-1}
30	25.22
40	23.04
50	21.17
60	20.07
70	18.57

Table 5. Effect of various PTC's on the rate of reaction: 2.5 g of K_2CO_3, 0.5 mL H_2O, 0.2 g of biphenyl (internal standard), 6 g of β-naphthol, 1 g of ethyl 2-bromoacteate, 0.2 g of PTC, 30 mL of chlorobenzene, 600 rpm, 50 ^{0}C, 40 kHz, 300 W

PTCs (g)	$k_{app} \times 10^3$, min^{-1}
TBPB	26.42
TBAB	25.22
TBAI	20.87
TBAHS	20.67
TBAC	16.13

conversions were observed to decrease. If much more water was added to the system, the overall reactions were no longer of the solid-liquid phase type [40]. In solid-liquid system, the addition of small amount of water can be useful in forming the catalytic intermediate for conducting intrinsic reactions.

5. Conclusions

In conclusion, the synthesis of ethyl 2-(naphthalen-2-yloxy)acetate in solid-liqiud heterogeneous condition under tetra-n-butylammonium bromide and ultrasonication was reported. The enhanced rate of reaction was obtained under sonication and PTC. The apparent reaction rates were observed to obey the pseudo-first order kinetics. The reaction mechanism and the apparent rate constants were obtained from the experimental results. The apparent rate constants are found to be directly dependent on each kinetic variables, viz., concentration of PTC, amount of K_2CO_3, ultrasonic frequencies, stirring speed, concentration of ethyl 2-bromoacetate and temperature. However it decreases with increase in the volume of water and volume of chlorobenzene. Energy of activation was calculated from the Arrhenius plot.

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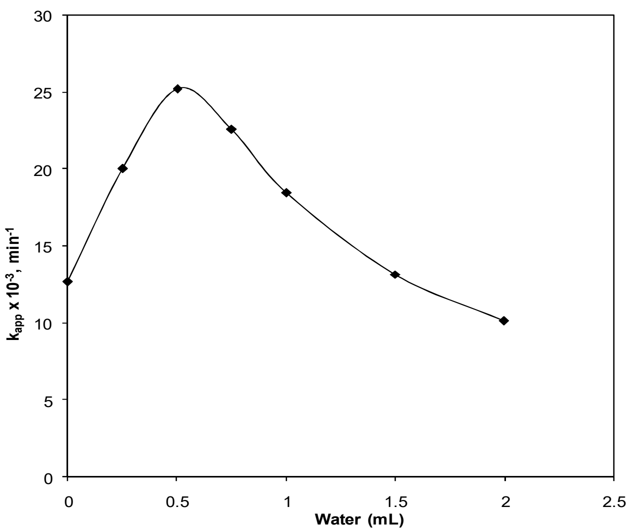

Figure 5. Effect of volume of water on k_{app}. Condition: 2.5 g of K_2CO_3, 0.2 g of biphenyl (internal standard), 6 g of β-naphthol, 1 g of ethyl 2-bromoacteate, 0.2 g of TBAB, 30 mL of chlorobenzene, 50 ^{0}C, 600 rpm, 40 kHz, 300 W

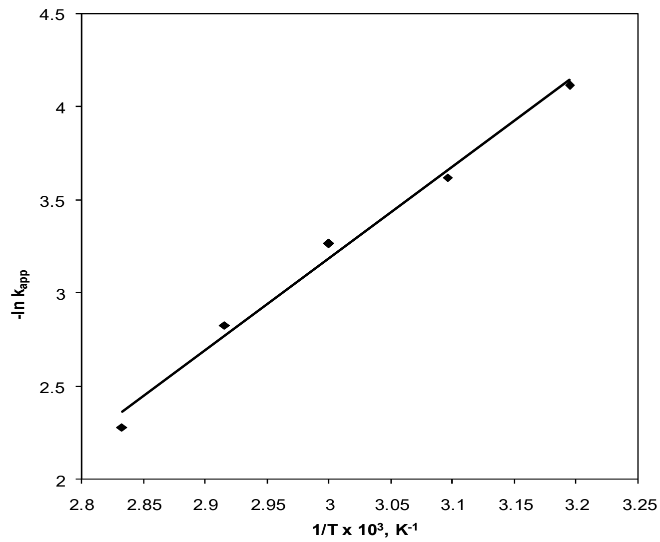

Figure 6. Arrhenius plot. Conditions: 2.5 g of K_2CO_3, 0.5 mL H_2O, 0.2 g of biphenyl (internal standard), 6 g of β-naphthol, 1 g of ethyl 2-bromoacteate, 0.2 g of TBAB, 30 mL of chlorobenzene, 600 rpm, 40 kHz, 300 W

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