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Ultrasound assisted the preparation of 1-butoxy-4-nitrobenzene under a new multi-site phase-transfer catalyst – Kinetic study

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1. Introduction

As the chemical reactants reside in immiscible phases, phasetransfer catalysts have the ability to carry out the heterogeneous reactions by one of the reactants penetrating from its normal phase (generally aqueous phase) to the organic phase where the reaction take place, which gives a high conversion and selectivity for the desired product under mild reaction conditions [1]. Ever since Jarrouse [2] found that quaternary onium salts as an effective catalyst for enhancing the two-phase reaction, this methodology occupies an unique niche in organic synthesis and it is a commercially matured discipline with over 600 applications [3-7] covering a wide spectrum of industries such as pharmaceuticals, agrochemicals, dyes, perfumes, flavours, specialty polymers, pollution control, etc. As the application of phase-transfer catalysts (PTC) grew, much effort was placed on the development of phase-transfer catalysts with higher catalytic efficiency. To this end, researchers have developed "multi-site" phase-transfer catalysts (MPTC) for much higher activity than normal phase-transfer catalysts. Recently, the catalytic behaviour of multi-site phase-transfer catalysts have been attracted much attention, due to the fact that multiple molecules of the aqueous reactant can be carried into the organic phase once a reaction cycle, thus the catalytic efficiency is enhanced [8-12].

ABSTRACT

In the present research work deals with the preparation of 1-butoxy-4-nitrobenzene was successfully carried out by 4-nitrophenol with *n*-butyl bromide using aqueous potassium carbonate and catalyzed by a new multi-site phase-transfer catalyst (MPTC) viz., N^1, N^4 -diethyl- N^1, N^1, N^4 -tetraisopropylbutane-1,4-diammonium dibromide, under ultrasonic (40 kHz, 300 W) assisted organic solvent condition. The pseudo first-order kinetic equation was applied to describe the overall reaction. Under ultrasound irradiation (40 kHz, 300 W) in a batch reactor, it shows that the overall reaction greatly enhanced with ultrasound irradiation than without ultrasound. The present study provides a method to synthesize nitro aromatic ethers by ultrasound assisted liquid-liquid multi-site phase-transfer catalysis condition.

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Currently, a new analytical and process experimental techniques which are environmental being techniques viz., ultrasound and microwave irradiation have become immensely popular in promoting various organic reactions [13–17]. Ultrasound irradiation is a transmission of a sound wave through a medium and is regarded as a form of energy enhance the rate of the reaction due to mass transfer and effective mixing [18–20].

The effect of ultrasonic energies in organic syntheses (homogeneous and heterogeneous reactions) has been boosted in recent years [21–27]. Sonication of multiphase systems accelerates the reaction by ensuring a better contact between the different phases [28,29]. Further, ultrasound irradiation also increase the reaction rate and avoid the use of high reaction temperatures [30]. These days this environmental benign technology is combined with phase-transfer catalysts (PTC) with primary objective of optimizing reaction conditions [31–33].

Our interest was entered on first time evaluating the influence of ultrasound in association with multi-site phase-transfer catalyst (MPTC) on the synthesis of 1-butoxy-4-nitrobenzene from 4-nitrophenol with *n*-butyl bromide (BB) under heterogeneous condition. Since, the kinetic study of O-alkylation of 4-nitrophenol using *n*-butyl bromide under controlled MPTC reaction conditions will be interesting and challenging, we followed the kinetic study using a newly synthesized multi-site phase-transfer catalyst (MPTC) viz., N^1 , N^4 -diethyl- N^1 , N^1 , N^4 -tetraisopropylbutane-1,4diammonium dibromide, as a catalyst under ultrasonic condition (40 kHz; 300 W). Further, to the best of our knowledge, there is



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no literature reports' regarding *n*-butylation of 4-nitrophenol under MPTC–ultrasonic irradiation condition.

2. Experimental

2.1. Chemicals

All reagents, including 4-nitrophenol, *n*-butyl bromide, potassium carbonate, benzene, toluene, chlorobenzene, biphenyl and other reagents are synthesis guaranteed grade (GR) chemicals and were used as received without further purification.

2.2. Instrumentation

FT-IR Spectra were recorded on a Brucker-Tensor 27 FT-IR spectrophotometer. ¹H NMR and ¹³C spectra were recorded on a Bruker 400 and 100 MHz respective using TMS as an internal standard. Gas chromatography was carried out using a GC-Varian 3700 model. Ultrasonic water bath, Equitron, Medica Instrument Manufacturing company, Chennai 600 004, India.

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 $48 \times 28 \times 20$ cm with liquid holding capacity of 5 L. Two types of frequencies of ultrasound were used in these experiments, which are 28 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 corner 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.

4. Synthesis of a new MPTC

A mixture of 4 g of *N*-ethyl-*N*-isopropylpropan-2-amine, 3.5 mL of 1,4-dibromobutane, and 60 mL of ethanol was placed in a 250 mL three necked round-bottomed Pyrex flask. The reaction mixture was refluxed in the nitrogen atmosphere for 48 h. The solvent and excess 1,4-dibromobutane were completely removed under vacuum and onium salt, i.e. N^1, N^4 -diethyl- N^1, N^1, N^4, N^4 -tetraisopropylbutane-1,4-diammonium dibromide (MPTC, Scheme 1) was washed with *n*-hexane (3 × 20 mL). The white solid MPTC (hygroscopic) was stored in a CaCl₂ desiccator. m.pt. 181 °C; Yield: 93%; FT-IR: 1180 cm⁻¹ (C-N⁺ stretching); ¹H NMR (400 MHz, CDCl₃); δ . 1.41–1.55 (m, 30H–CH₃), 1.99 (s, 4H, CH₂), 3.07–3.14

(m, 8H, N⁺–CH₂) 3.63–3.71 (m, 4H, CH); ¹³C NMR (100 MHz, CDCl₃): δ . 12.19 (CH₃), 17.40 (CH₃), 18.68 (CH₂), 42.51 (N⁺–CH₂), 54.25 (N⁺–CH).

5. Synthesis of 1-butoxy-4-nitrobenzene under mechanical stirring

To the mixture of K₂CO₃ (20 g, 0.1449 mol) in water (15 mL) and the newly synthesized MPTC (0.6 g, 1.2658×10^{-3} mol), 4-nitrophenol (0.5 g, 3.5×10^{-3} mol) was added under overhead stirring to generate the phenoxide anion. Then *n*-butyl bromide $(0.5913 \text{ g}, 4.3 \times 10^{-3} \text{ mol})$ in chlorobenzene (40 mL) was added slowly. The reaction mixture was heated at 65 °C for 6 h with vigorous stirring. The crude product was isolated by simple extraction with diethyl ether (3 \times 25 mL). The organic layer was collected and the solvent was evaporated under reduced pressure. The crude product was chromatographic (SiO₂) employing hexane:ethyl acetate (9:1) as an eluent to obtain a pure monoderivative. The identity of the product was confirmed by ¹H NMR and ¹³C NMR spectra of the product. m.pt. 306-308 °C; Yield: 88%; ¹H NMR (400 MHz, CDCl₃): δ . 0.96–0.98 (t, 3H, CH₃), 5.34–1.33–1.45 (m, 2H, CH₂), 1.71-1.86 (m, 2H, CH₂), 3.90-4.01 (t, 3H, CH₃), 7.13, 8.18 (m, 4H, Ar-CH). ¹³C NMR (100 MHz, CDCl₃): δ. 14.12 (CH₃), 19.16 (CH₃), 32.01 (CH₂), 68.67 (CH₂), 115.31, 121.72, 140.05, 163.64 (Ar-CH).

6. Reaction mechanism and kinetic model

For synthesizing 1-butoxy-4-nitrobenzene compound, the overall reaction of 4-nitrophenol and *n*-butyl bromide (BB) was catalysed by the newly prepared MPTC (Q^+Br^-) in the aqueous alkaline (K_2CO_3) bi-phase medium and is represented in Scheme 2. The reaction is carried out under MPTC assisted ultrasonic irradiation condition. In the current investigation the kinetics was followed in the presence of an excess amount of 4-nitrophenol and by fixing *n*-butyl bromide as limiting agent. The main reason for investigating this reaction is, the effect of low frequency ultrasound irradiation (40 kHz, 300 W) along with agitation speed (600 rpm) to find out the effect of change of k_{app} value of this system.

6.1. Definition

The conversion (X) of *n*-butyl bromide (BB) is defines as follows: $X = 1 - \{ [BB]_0 / [BB]_{0i} \}$ (1)

where $[BB]_0$ and $[BB]_{0,i}$ represent the concentration of butyl bromide at time (*t*) *t* = 0 and *t* > 0, respectively.

6.2. Rate expression

The rate expression for this reaction may be expressed as:



N-ethyl-N-isopropylpropan-2-amine N^1, N^4 -diethyl- N^1, N^1, N^4, N^4 -tetraisopropylbutane-1,4-diaminium

dibromide

Scheme 1. Preparation of MPTC.

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(Preparation of 1-butoxy-4-nitrobenzene)



Scheme 2. Preparation of 1-butoxy-4-nitrobenzene.

 $-r_{\rm BB} = k_{\rm app} [\rm BB]_0 \tag{2}$

where k_{app} is the apparent reaction rate constant. This reaction is carried out in a batch reactor, so the diminution rate of BB with time (*t*) can we expressed as:

 $-d[BB]_0/dt = -r_{BB} = k_{app}[BB]_0$ (3)

on integrating Eq. (3) yields:

 $-\ln\{[BB]_0/[BB]_{0,i}\} = -\ln(1-X) = k_{app}$ (4)

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

7. Results and discussion

The reaction was conducted on a 150 mL three-necked Pyrex round-bottom flask which permits agitating the solution, inserting the water condenser to recover organic reactant and taking samples and feeding the reactants. This reaction vessel was suspended at the centre of the sonicator. A known quantity of chlorobenzene (30 mL, solvent), potassium carbonate (20 g, 0.1447 mol), 0.2 g biphenyl IS. (internal standard) were introduced into the reactor. Then, 0.5 g of 4-nitrophenol (3.6×10^{-3} mol) and 0.4 g of *n*-butyl bromide $(2.72 \times 10^{-3} \text{ mol})$, 0.3 g of the newly synthesized MPTC (with respect to *n*-butyl bromide, limiting reagent) 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 of the mixture (by stopping the stirring for 20-30 s each time) at regular time intervals. A pinch of anhydrous CaCl₂ was placed in the sample vials to absorbs any moisture present in the organic layer. Each run consisted of six samples taken over the period ranging from 5 to 30 min. The kinetics was followed by estimating the amount of butyl bromide (limiting reagent) that disappeared using a gas Chromatography (GC-Varian 3700 model). The analyzing conditions were as follows; Column, $30 \text{ m} \times 0.525 \text{ mm}$ i.d. capillary column containing 100% poly(dimethyl siloxanen); injection temperature, 250 °C; FID detector (300 °C). Yields were determined from standard curve using biphenyl as an internal standard.

7.1. Combined effect of ultrasound and mechanical stirring on the reaction

To ascertain the influence of agitation speed on the rate of *n*-butylation of 4-nitrophenol, the speed of agitation was varied in the range of 100–1000 rpm along with ultrasound irradiation (40 kHz, 300 W) using N^1 , N^4 -diethyl- N^1 , N^1 , N^4 -tetraisopropylbutane-1,4-diammonium dibromide (MPTC). The result indicates that the rate of the reaction increases linearly as the agitation speed increases from 100 to 600 rpm (Fig. 1). However, on further increasing the agitation seed from 600 to 1000 rpm, there is no



Fig. 1. Plot of the apparent rate constant versus various stirring speeds; 0.5 g of 4nitrophenol 20 g of K_2CO_3 , 15 mL of H_2O , 0.2 g of internal standard (biphenyl), 0.6 g of butyl bromide, 0.3 g of MPTC, 30 mL of chlorobenzene, 65 °C; ultrasound conditions (40 kHz, 300 W).

significant improvement in the reaction rate constant. This is because the interfacial area per unit volume of dispersion increased linearly with increasing the stirring speed till 600 rpm is reached, where there is no significant increase in the interfacial area per unit volume of dispersion with the corresponding increase in the speed. Thus, increasing the stirring speed changes the particle size of the dispersed phase. Therefore, the agitation speed was set at 600 rpm for studying the reaction phenomena from which the resistance of mass transfer stays at a constant value [34–42]. The k_{app} values are evaluated from the linear plot of $-\ln(1 - X)$ versus time. The results indicate that the mechanical effects brought up by the use of low frequency ultrasounds are responsible of the enhancement of the kinetics by harsh mixing, enhancement of mass transfer and so on further, when the same reaction was carried out in the absence of ultrasound, the observed k_{app} value (0 kHz: $k_{app} = 5.12 \times 10^{-3} \text{ min}^{-1}$) almost five fold lesser than in the presence of ultrasonication (40 kHz: $k_{\rm app} = 26.72 \times 10^{-3} \, {\rm min}^{-1}$).

7.2. Effect of the amount of newly prepared MPTC

Experiments were conducted by varying the amount of the newly synthesized MPTC viz., N^1, N^4 -diethyl- N^1, N^1, N^4, N^4 -tetra-

isopropylbutane-1,4-diammonium dibromide by keeping other experimental parameters are kept constant. The influence of the amount of MPTC on the O-alkylation of 4-nitrophenol has been studied by varying amount of MPTC from 0.2 to 1.0 g under ultrasound irradiation (40 kHz, 300 W). Apparent rate constants were evaluated from the plot of $-\ln(1 - X)$ versus time. As shown in Fig. 2, the rate of the reaction increased with increasing in the amount of MPTC along with ultrasound irradiation (40 kHz, 300 W). The k_{app} values are linearly dependent on the amount of multi-site phase-transfer catalyst. The increasing the k_{app} value is attributed to the positive effect of ultrasound might be enlarged [43].

7.3. Effect of the concentration of n-butyl bromide

To investigate the influence of *n*-butyl bromide (BB) on the kinetics of synthesis of 1-butoxy-4-nitrobenzene under ultrasonic irradiation condition (40 kHz, 300 W), the amount of BB was varied from 0.2 to 1.0 g. In the presence and absence of ultrasound results are shown in (Table 1). The data clearly indicates that the $k_{\rm app}$ value increases with increasing the amount of *n*-butyl bromide. When the *n*-butyl bromide concentration increased, the probability of finding the substrate with active-site of the catalyst and ultrasound enhanced the rate of the reaction [43,44]. It may be due to reduces the surface area between the aqueous and organic phases, and hence more reactants collide to each other simultaneously we get higher $k_{\rm app}$ value.

7.4. Effect of temperature

The effect of temperature on the reaction between 4-nitrophenol and *n*-butyl bromide was studied under otherwise similar conditions. The temperature was varied from 30 to 80 °C. The kinetic profile of the reaction is obtained by plotting $-\ln(1 - X)$ versus time. It is obvious that the reactivity is increased with an increase in the temperature along with ultrasonic effect



Fig. 2. Effect of the amount of MPTC on the apparent rate constant: 0.5 g of 4-nitrophenol 20 g of K_2CO_3 , 15 mL of H_2O , 0.2 g of internal standard (biphenyl), 0.6 g of butyl bromide, 0.3 g of MPTC, 30 mL of chlorobenzene, 65 °C; ultrasound conditions (40 kHz, 300 W).

[45]. The reason is that the number of reactant molecules which possess higher activation energy at a higher temperature and thus the ultrasonic wave easily passes through the reactor [46,47]. The other point is that the collision of the reactants at higher temperature is also increased. Hence, the apparent rate constant is increased at higher temperature. Arrhenius plots were made in Fig. 3 of $-\ln k_{app}$ against 1/T to get activation energy of 52.16 kJ mol⁻¹.

From the literature survey, the dehydrobromination of (2bromoethyl)benzene catalyzed by tetraoctylammonium bromide (TOAB), an extraction mechanism was proposed [48] due to lower $E_{\rm a}$ value (<43 kJ mol⁻¹). In general, higher activation energy (more than 43 kJ mol⁻¹) suggest an interfacial mechanism [44,49]. The activation energy for the heterogeneous ethylation of phenylactonitrile was reported to be 63.64 kJ mol⁻¹ and for this an interfacial mechanism was proposed [10]. Further, in the N-alkylation of pyrrolidine-2-one, the E_a (51.35 kJ mol⁻¹) was reported by Sasson and Bilman [50], and for this reaction they proposed an interfacial mechanism. They concluded that the deprotonation of the substrate takes place at the interphase and consequently the organic anion is extracted and reacts in the bulk of the organic phase. The rate-determining step in the process is the anion exchange at the interphase. In our study, the observed E_a value is 52.36 kJ mol⁻¹. Hence, we proposed an interfacial mechanism for our present study [44,51,52].

7.5. Influence of amount of water

n-Butylation of 4-nitrophenol with *n*-butyl bromide as a limiting agent under ultrasound condition (40 kHz, 300 W) was examined by varying the amount of water from 30 to 50 mL, under standard reaction conditions. Apparent rate constants were obtained from the plot of $-\ln(1 - X)$ against time. Generally, the volume of water directly affects both the concentration of potassium carbonate in the aqueous phase and also generation of anions. Therefore, the conversion (or the reaction rate) will be affected by the volume of water. Fig. 4 shows the effect of the amount of water on the rate of the reaction. On increasing the volume of water, the concentration of alkali compound in aqueous solution is decreases. This situation would dramatically reveal the hydration effect of the active catalyst [PhO⁻Q⁺] as the volume of water changed from 30 to 50 mL. From the literature, the kinetic study of the phase-transfer catalyzed etherification of 4,4'-bis(chloromethyl)-1,1'-biphenyl with phenol in an alkaline solution of potassium hydroxide/organic solvent two-phase medium, similar decrease in rate of the reaction on corresponding increase in volume of water was reported [53].

7.6. Effect of ultrasonic power

Ultrasonic irradiation is defines as acoustic waves with frequencies in the 20–100 MHz range [24,54]. They create cavities generating locally high temperature and pressures [55–58] or strong electric fields [56,58–60]. Ultrasound is known to accelerate diverse types of organic reactions and it is established generous reactions, which are otherwise slow due to poor mass transfer are accelerated by sonication due to cavitation [57]. It has been reported that a combination of PTC and ultrasound is often better than either of the two techniques alone [58]. In such transfer of species across the interface and ultrasound merely facilitates this transfer, possibly by increasing the interfacial area across which this transfer occurs.

To ascertain the influence of various ultrasonic frequencies on the rate of *n*-butylation of 4-nitrophenol with same output power of 300 W, the ultrasonic frequency was varied in the range of 28 and 40 kHz under otherwise similar conditions using MPTC as the catalyst. Also we followed the reaction under silent condition.

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Table 1

Effect of amount of *n*-butyl bromide (BB) on the rate of *n*-butylation of 4-nitrophenol under ultrasonic condition: 20 g of K₂CO₃, 15 mL of H₂O, 0.2 g of internal standard (biphenyl), 0.3 g of MPTC, 30 mL of chlorobenzene, 600 rpm, 65 °C; ultrasound conditions (40 kHz, 300 W).

| Effect of the amount of <i>n</i> -butyl bromide | | | | |
|---|---|---|--|--|
| Butyl bromide (BB) (g) | $k_{ m app} 	imes 10^3 { m min}^{-1}$ (with ultrasound, 40 kHz, 300 W) | $k_{ m app} 	imes 10^3 { m min}^{-1}$ (without ultrasound) | | |
| 0.2 | 17.68 | 3.08 | | |
| 0.4 | 21.44 | 4.66 | | |
| 0.6 | 26.72 | 5.12 | | |
| 0.8 | 31.82 | 6.02 | | |
| 1.0 | 36.41 | 7.22 | | |



Fig. 3. Arrhenius plot; 0.5 g of 4-nitrophenol 20 g of K_2CO_3 , 15 mL of H_2O , 0.2 g of internal standard (biphenyl), 0.6 g of butyl bromide, 0.3 g of MPTC, 30 mL of chlorobenzene, 65 °C; ultrasound conditions (40 kHz, 300 W).

The kinetic profile of the reaction is obtained by plotting $-\ln(1 - X)$ against time. In our experimental condition at 30 minutes, without ultrasonic irradiation the k_{app} values is $5.12\times 10^{-3}\,min^{-1}$ but in the presence of ultrasonic condition the $k_{\rm app}$ values are 16.26×10^{-3} and $26.72 \times 10^{-3} \, {\rm min}^{-1}$ for 28 kHz (300 W) and 40 kHz (300 W), respectively Table 2. The reaction rate with ultrasound irradiation (40 kHz, 300 W) was about five times of that without using ultrasound. It may be due to the mixing of organic and aqueous phases increased in the heterogeneous reaction i.e. the heterogeneous system may act as homogeneously in the presence of ultrasonication. Hence, we get higher k_{app} value compared with conventional method [57-62]. In addition, different ultrasonic frequencies induce various degrees of "cavity factor". Hence, the overall $k_{\rm app}$ was increased by increasing the ultrasonic frequency in the order of 0 < 28 (300 W) < 40 kHz (300 W) for our system. Similar trend was observed by Entezari et al. [61,62].

7.7. Effect of organic solvents

In this work, the influence of various organic solvents on the rate of *n*-butylation of 4-nitrophenol was followed under otherwise standard reaction conditions. Five organic solvents employed in this study are toluene, anisole, cyclohexane, chlorobenzene, and benzene. From the plot of $-\ln(1 - X)$ against time, the k_{app} values are shown in the Table 3. From the Table 3, chlorobenzene



Fig. 4. Plot of the apparent rate constants versus different volumes of water; 0.5 g of 4-nitrophenol 20 g of K_2CO_3 , 15 mL of H_2O , 0.2 g of internal standard (biphenyl), 0.6 g of butyl bromide, 0.3 g of MPTC, 30 mL of chlorobenzene, 65 °C; ultrasound conditions (40 kHz, 300 W).

Table 2

Influence of ultrasonic frequencies on the rate of *n*-butylation of 4-nitrophenol under ultrasonic condition: 20 g of K₂CO₃, 15 mL of H₂O, 0.2 g of internal standard (biphenyl), 0.3 g of MPTC, 0.6 g butyl bromide, 30 mL of chlorobenzene, 600 rpm, 65 °C.

| Effect of ultrasonic frequency | | | |
|---|------|-------|-------|
| Ultrasonic frequency (kHz, 300 W) | 0 | 28 | 40 |
| $k_{\rm app} 	imes 10^3 \ ({\rm min}^{-1})$ | 5.12 | 16.26 | 26.72 |

possesses a higher k_{app} value among the five organic solvents, due to its higher dielectric constant. In another view the ultrasonic irradiation can enhance the rate in the presence of more polar solvents due to passing higher ultrasonic waves to the reactor and makes fruitful collision between the reactants, and hence we get higher k_{app} value for chlorobenzene solvent of this system and also this statement is not always true [63–65].

7.8. Effect of varying potassium carbonate concentrations

In the PTC/base catalyzed reactions, the reaction rate is known to be greatly affected by a concentration of the alkaline compound.

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Table 3

Influence of organic solvents on the rate of *n*-butylation of 4-nitrophenol under ultrasonic condition: 20 g of K₂CO₃, 15 mL of H₂O, 0.2 g of internal standard (biphenyl), 0.3 g of MPTC, 0.6 g butyl bromide, 600 rpm, 65 °C; ultrasound conditions (40 kHz, 300 W).

| Effect of organic solvents | rganic solvents | | | | |
|--|-----------------|---------|---------|---------|---------------|
| | Solvents | | | | |
| | Cyclohexane | Benzene | Toluene | Anisole | Chlorobenzene |
| ε^{a} (dielectric constant) | 2.02 | 2.28 | 2.31 | 4.30 | 5.60 |
| $k_{\rm app} 	imes 10^3 \ ({ m min}^{-1}) \ ({ m with ultrasound, 40 \ kHz, 300 \ W})$ | 12.72 | 14.58 | 18.05 | 23.62 | 26.72 |
| $k_{\rm app} \times 10^3 ({ m min}^{-1})$ (without ultrasound) | 2.33 | 2.91 | 3.63 | 4.22 | 5.12 |

Table 4

Influence of alkalinity on $k_{\rm app}$ in the *n*-butylation of 4-nitrophenol under ultrasonic condition: 0.2 g of internal standard (biphenyl), 0.3 g of MPTC, 0.6 g butyl bromide, 30 mL of chlorobenzene, 600 rpm, 65 °C; ultrasound conditions (40 kHz, 300 W).

| Effect of organic solvents | | | | |
|---|--|--|--|--|
| $k_{ m app} 	imes 10^3 \ (min^{-1}) \ (with ultrasound, 40 \ kHz, 300 \ W)$ | $k_{ m app} 	imes 10^3 \ ({ m min}^{-1}) \ ({ m without \ ultrasound})$ | | | |
| 16.22 | 3.09 | | | |
| 20.91 | 4.23 | | | |
| 26.72 | 5.12 | | | |
| 30.46 | 6.02 | | | |
| 34.33 | 6.76 | | | |
| | $\frac{\text{nic solvents}}{k_{\text{app}} \times 10^3 \text{ (min}^{-1}) \text{ (with ultrasound, 40 kHz, 300 W)}}$ 16.22 20.91 26.72 30.46 34.33 | | | |

The rate of O-alkylation of 4-nitrophenol strongly depends on the strength of the potassium carbonate. Kinetic experiment were carried out, by employing 20-40 g of K_2CO_3 under similar reaction conditions. The Kinetic profile of the reaction is obtained

by $-\ln(1 - X)$ against time. The k_{app} values tremendously increased with increasing in basicity of CO_3^{2-} ion (Table 4). It suggest that the carbonate ions which are less solvated by water molecules and there by the k_{app} value increases [66,67].

8. Mechanism

Generally mechanism [41,67,68] for basic anion initiated PTC reactions are classified into two types viz.: (i) Starks extraction mechanism and (ii) Maksoza interfacial mechanism. In the extraction mechanism is more likely to be part of reactions when they depend agitation speed only up to certain level (300 rpm) and there after the rate will be constant factor. Also the energy of activation calculated from the Arrhenius plot will be below 45.36 kJ mol⁻¹, on the other hand, if the reaction in interfacial driven reaction the rate of the reaction keep on increasing even after 300 rpm and energy activation will be above 45.36 kJ mol⁻¹.

(Reaction mechanism)



Scheme 3. Reaction mechanism.

The experimental results from the present kinetic study indicates that the dependencies of the kinetic data on the entire stirring speed, concentration of the MPTC, aqueous potassium carbonate (K_2CO_3), temperature and higher E_a value are indicative of an interfacial mechanism. Therefore we proposed an interfacial mechanism according to the literature [41,67,68] as well as the k_{app} value of the present investigation (Scheme 3). In this study, initially the carbonate anion deprotonates 4-nitrophenol at the interface, forming an ion-pair viz., potassium phenoxide (PhO⁻K⁺). Upon the addition of multi-site phase-transfer catalyst, Q⁺X⁻, an ion exchange takes place between the ion-pair $(PhO^{-}K^{+})$ and $Q^{+}X^{-}$ at the interface and we get the newly formed ion-pair $PhO^{-}Q^{+}$, which is more organophilicity than either $PhO^{-}K^{+}$ or Q⁺X⁻ and hence PhO⁻Q⁺ easily migrates into the organic phase. This ion-pair (PhO^{$-Q^+$}) reacts with the alkylating agent viz., *n*-butyl bromide (BB) in the organic phase resulting in the formation of the required product i.e. 1-butoxy-4-nitrobenzene along with O⁺Br⁻. The quaternary bromide salt (Q⁺Br⁻) formed in the organic phase migrates into the aqueous phase due to its hydrophilicity nature. This cyclic process going on up to the disappearance of *n*-butyl bromide (limiting agent) present in the organic phase.

9. Conclusion

In the present study, the rate of the reaction was controlled to study the kinetic aspects of the formation of the 1-butoxy-4-nitrobenzene from 4-nitrophenol and *n*-butyl bromide under ultrasonic-MPTC condition. The apparent reaction rates were observed to obey the pseudo-first order kinetics, performing the reaction in ultrasonic condition resulted in shorter reaction time, selectivity, high yield, etc. 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., [MPTC], [K₂CO₃], ultrasonic frequency, stirring speed and temperature. However it decreases with increase in volume of water. Energy of activation was calculated from the Arrhenius plot. Based on the experimental evidence, an interfacial mechanism has been proposed. Combination of ultrasound and MPTC resulted in better efficacy as compared to the individual operations.

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