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Ultrasound assisted arylation of benzyl alcohol with 4-nitrochlorobenzene under a new multi-site phase-transfer catalyst in solid–liquid condition

Varathan Selvaraj [a], Pachaiyappan Abimannan [a], Venugopal Rajendran [b,*]

[a] Pachaiyappa's College for Men, Kanchipuram 631 501, Tamil Nadu, India
[b] Department of Chemistry, Pachaiyappa's College for Men, Kanchipuram 631 501, Tamil Nadu, India

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ABSTRACT

The ultrasound assisted preparation of 1-(benzyloxy)-4-nitrobenzene from the reaction of 4-chloronitrobenzene (CNB) and benzyl alcohol was carried out successfully using potassium hydroxide and catalyzed by a new multi-site phase-transfer catalyst (MPTC) viz., 1,3,5-triethyl-1,3,5-trihexyl-1,3,5-triazinane-1,3,5-triium trichloride in a solid–liquid reaction condition (SL-MPTC). The advantage of using SL-MPTC is to avoid a serious hydration of potassium salt of benzyl alcohol in the reaction between 4-chloronitrobenzene (CNB) and benzyl alcohol. The reaction is greatly enhanced in the solid–liquid system, catalyzed by multi-site quaternary ammonium salt (MPTC) and 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 reaction mechanism is proposed and verified by examining the experimental evidence. A kinetic model is proposed in which a pseudo first-order rate law is sufficient to describe the results, such as the effects of agitation speed, ultrasound, different phase transfer catalysts and the effect of organic solvents, the amount of newly prepared MPTC, the effect of temperature, the amount of water, the concentration of 4-chloronitrobenzene (CNB) and potassium hydroxide concentrations. The apparent rate constant (k_{app}) were investigated in detail. Rational explanations to account for the phenomena on the results were made.

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 [1–3]. 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. The recent trend towards "green and sustainable chemistry" has again attracted a strong attention to its significance for organic syntheses. Water some times interferes with the desired reaction through suppression or diversion. Thus, PTC was often carried out with solid reagent salts in the absence of water (solid–liquid PTC, (SLPTC)). In many solid–liquid systems, however, small quantities of water play an important role in the catalytic processes [2–5]. The catalytic reactions hardly proceeded under anhydrous conditions, thus the hydrolysis reaction can be effectively inhibited and the reaction rate can be promoted. SLPTC exhibits the advantages of easy separation of products, selection of organic solvents and prevention of unfavorable side reactions [6,7]. The most common operations are involve the liquid–liquid (L–L) mode of operation, in this operation PTC has been quite successful for C, N, O and S alkylation's involving SN^2 type reactions in fine chemical industries, apart from dehydrohalogenations. When the halogen exchange of alkoxide is conducted in liquid–liquid mode (L–L PTC), there is always a formation of alcohol due to hydrolysis. One of the ways to suppress by-product formation and also intensify the rates of reactions of L–L PTC is through the use of solid–liquid (S–L) PTC in which the aqueous phase promoted reactions can be totally suppressed and better selectivity obtained [8,9]. In SLPTC, the nucleophile reactant is in solid form (usually an alkali metal salt) and the other reactant exists in the organic solvent [10]. The role of the catalysts, which are usually quaternary ammonium salts, is to maintain the presence of reacting anions in the reaction medium [11]. Recently, in PTC, multi-site phase transfer catalyst shows significant enhancement in reaction rate

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* Corresponding author. Tel.: +91 44 9488439279; fax: +91 44 27268824.
E-mail addresses: selvarajptc@gmail.com (V. Selvaraj), abimannan01@gmail.com (P. Abimannan), rajendranv1967@gmail.com, venugopal.rajendran@ymail.com (V. Rajendran).

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[12]. The multi-site phase-transfer catalyst contains more than one active center, and has the potential to be used in solid–liquid system. The most significant merit for MPTC's is that it has an ability to transfer more number of anionic species (M^+Y^-) from aqueous or solid phase to organic phase. In contrast, the single-site quaternary onium phase-transfer catalyst can transfer only one molecule of anionic species, i.e., M^+Y^- from aqueous or solid phase per cycle. Especially, nowadays much emphasis has been given to economy of scale and efficiency of onium salts particularly for the industrial scale preparation of organic compounds. In our laboratory too, several multi-site phase transfer catalysts are reported for various reactions [13–15]. Ultrasonic irradiation in biphase reaction can increase interfacial area coupled with local hot-spot generation, and has been demonstrated to promote high reaction rate in organic synthesis [16–19]. 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 solid–liquid PTC has revealed significant improvement in the reaction rate. In solid–liquid PTC system, the overall reaction rate can also be effectively raised with or without multi-site phase-transfer catalyst [20–23]. But the application of ultrasound in SLPTC especially catalyzed by multi-site phase-transfer catalyst was rarely reported.

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-(benzyloxy)-4-nitrobenzene from potassium salt of benzyl alcohol with 4-chloronitrobenzene (CNB) under heterogeneous solid–liquid condition. Since, the kinetic study of arylation of benzyl alcohol using 4-chloronitrobenzene under controlled MPTC reaction conditions will be interesting, we followed the kinetic study using a newly synthesized multi-site phase-transfer catalyst (MPTC) viz., 1,3,5-triethyl-1,3,5-trihexyl-1,3,5-triazinane-1,3,5-triium trichloride, as a catalyst under ultrasonic condition (40 kHz; 300 W). Further, to the best of our knowledge, there is no literature report's regarding 4-nitrophenylation of benzyl alcohol under combined MPTC–ultrasonic irradiation condition. An alternative procedure (method II) also tried to get same product (1-(benzyloxy)-4-nitrobenzene) under a new MPTC assisted by ultrasound (40 kHz, 300 W) using 4-nitrophenol, benzyl chloride and potassium carbonate.

2. Experimental

2.1. Chemicals

All the reagents, including, benzyl alcohol, 4-chloronitrobenzene (CNB), benzyl chloride, 4-nitrophenol, ethylamine, paraformaldehyde, n-hexyl chloride, biphenyl, tetrabutylammonium chloride (TBAC), tetrabutylammonium bromide (TBAB), benzyltriethylammonium chloride (BTEAC), tetraethylammonium chloride (TEAC), tetraethylammonium bromide (TEAB), potassium hydroxide, potassium carbonate, n-hexane, toluene, chlorobenzene, anisole, diethyl ether and other reagents for synthesis were guaranteed grade (GR) chemicals and were used without further purification.

2.2. Instrumentation

^{1}H NMR and ^{13}C spectra were recorded on a Bruker 300 and 75 MHz respective using TMS as an internal standard. Gas chromatography was carried out using a GC-Varian 3700 model. Ultrasonic water bath, Equitron, Media Instrument Manufacturing Company, Chennai, India-600 004. The ultrasonic generator was a thermostatic bath equipped with dual frequencies (28/40 kHz) and electric power 300 W with 0.0126 W/mL of power density.

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 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 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. Synthesis of 1,3,5-triethyl-1,3,5-triazinane

A mixture of 83 g of ethylamine, and 40 g of paraformaldehyde were placed in a 250 mL three necked round bottomed Pyrex flask. The reaction was carried out at 40 °C for 4 h and was gently refluxed in the nitrogen atmosphere. After reaction completed the solvent was completely removed under vacuum and we get 1,3,5-triethyl-1,3,5-triazane (Scheme 1) the colorless liquid was stored in a refrigerator. Yield: 92%; ^{1}H NMR (300 MH$_Z$, CDCl$_3$); δ 1.054–1.102 (t, 9H–CH$_2$–C$\mathbf{H_3}$), 2.449–2.522 (q, 6H–C$\mathbf{H_2}$–CH$_3$), 3.432 (s, 6H, N–C$\mathbf{H_2}$). ^{13}C NMR (75 MH$_Z$, CDCl$_3$): δ 12.62 (CH$_2$–$\mathbf{C}$H$_3$), 46.50 ($\mathbf{C}$H$_2$–CH$_3$), 73.72 (N–$\mathbf{C}$H$_2$). Elemental analysis: Calculated: C, 62.98%; H, 12.16%; N, 24.23%; and Found: C, 63.11%; H, 12.36%; N, 24.53%.

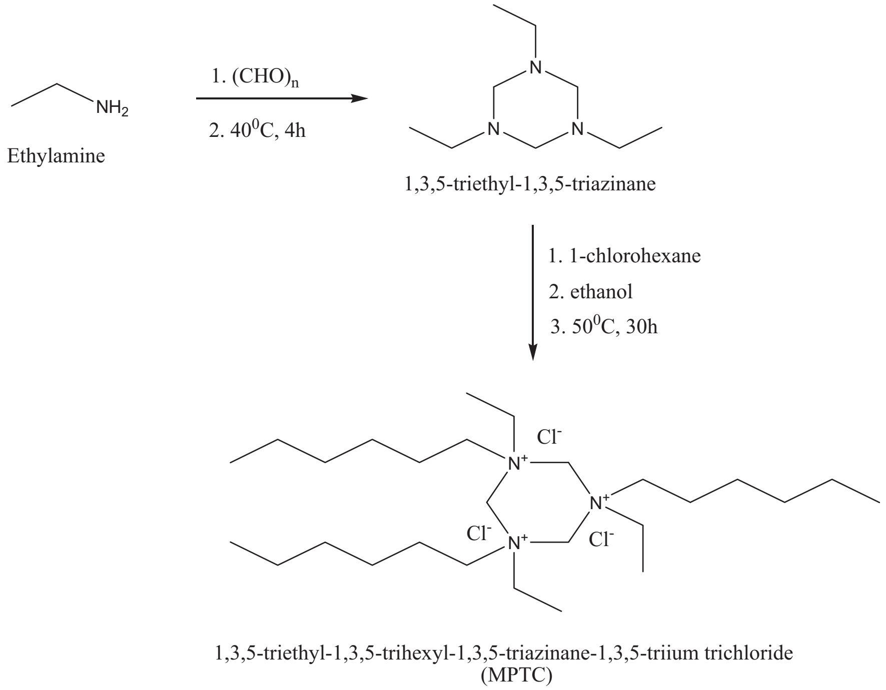
2.5. Synthesis of a new MPTC

A mixture of 8.7 g (50.7 mmol) of 1,3,5-triethyl-1,3,5-triazane, 29.4 g (24.9 mL, of hexyl chloride, and 80 mL of ethanol was placed in a 250 mL three necked round bottomed Pyrex flask. The reaction was carried out at 50 °C for 30 h and was gently refluxed in the nitrogen atmosphere. The solvent was then completely removed under vacuum and the onium salt, i.e., 1,3,5-triethyl-1,3,5-trihexyl-1,3,5-triazinane-1,3,5-triium trichloride, (MPTC; Scheme 1) was washed with n-hexane (4 × 25 mL). The Brownish oily liquid was stored in CaCl$_2$ desiccator. Yield: 96%; ^{1}H NMR (300 MH$_Z$, CDCl$_3$); δ 0.8(t, 9H, –C$\mathbf{H_3}$ in hexyl group), 1.088–1.136 (t, 9H, –C$\mathbf{H_3}$ in ethyl group), 1.168–1.367 (m, 24H, –C$\mathbf{H_2}$ in hexyl group), 2.585–2.622 (t, 6H, N$^+$–C$\mathbf{H_2}$ in hexyl group), 3.302–3.398 (q, 6H, N$^+$–C$\mathbf{H_2}$ in ethyl group), 5.203 (s, 6H, N$^+$–C$\mathbf{H_2}$–N$^+$) ^{13}C NMR (75 MH$_Z$, CDCl$_3$): δ 5.5(–$\mathbf{C}$H$_3$ in hexyl group), 13.40 (–$\mathbf{C}$H$_3$ in Ethyl group), 21.81 (N$^+$–CH$_2$–$\mathbf{C}$H$_2$), 23.25 ($\mathbf{C_5}$**-** in hexyl group), 26.55 ($\mathbf{C_3}$**-** in hexyl group), 30.52($\mathbf{C_4}$**-** in hexyl group), 51.58(N$^+$–$\mathbf{C}$H$_2$ in ethyl group), 69.55 (N$^+$–$\mathbf{C}$H$_2$ in hexyl group); Elemental analysis: Calculated: C, 60.86%; H, 11.42%; Cl, 19.10%; N, 7.92%; and Found: C, 60.83%; H, 11.34%; Cl, 19.95%; N, 7.88%.

3. Synthesis of 1-(benzyloxy)-4-nitrobenzene under mechanical stirring

3.1. Method-I

To the well powdered KOH (10 g) 1 mL of water and (1.0 g, 9.25 mmol) of benzyl alcohol was added under overhead stirring for few minutes to generate the benzyl alcohol anion. Then 4-chloronitrobenzene (1 g, 6.35 mmol) and the newly synthesized MPTC (0.3 g) in chlorobenzene (30 mL) were added slowly. The



Scheme 1. Preparation of MPTC.

reaction mixture was heated at 60 °C for 2 h with vigorous stirring. The product formed was evidenced by Thin Layer Chromatography (TLC). The crude product was isolated by simple extraction with ethyl acetate (3 × 25 mL). The organic layer was collected and the solvent was evaporated under reduced pressure. The crude product was subjected to chromatography (SiO_2) employing hexane: ethyl acetate (9:1, v/v) as an eluent to obtain a pure (1-(benzyloxy)-4-nitrobenzene; Scheme 2) in the form of colorless solid. The identity of the product was confirmed by ^{1}H NMR and ^{13}C NMR spectra of the product. The Melting point of the compound (1-(benzyloxy)-4-nitrobenzene) is 90–92 °C; ^{1}H NMR (300 $\mathrm{MH_Z}$, $CDCl_3$): δ 5.131(s, 2H, –C**H**$_2$), 6.980–7.010 (d, 2H, 4-chloronitrobenzene Ar–C**H**-near to O-linkage), 7.346–7.438 (m, 5H, benzyl Ar–C**H**), 8.140–8.169 (d, 2H, 4-nitrochlorobenzene Ar–C**H**-near to –NO_2 group); ^{13}C NMR (75 $\mathrm{MH_Z}$, $CDCl_3$): δ. 70.71 (–**C**H$_2$), 114.90, 125.94, 127.56, 128.53, 128.84, 135.59, 141.66, 163.75 157.46 (Ar–**C**arbon); Elemental analysis: Calculated: C, 68.18%; H, 4.87%; N, 6.15%; O, 20.98% and Found: C, 68.11%; H, 4.84%; N, 6.11%; O, 20.94%

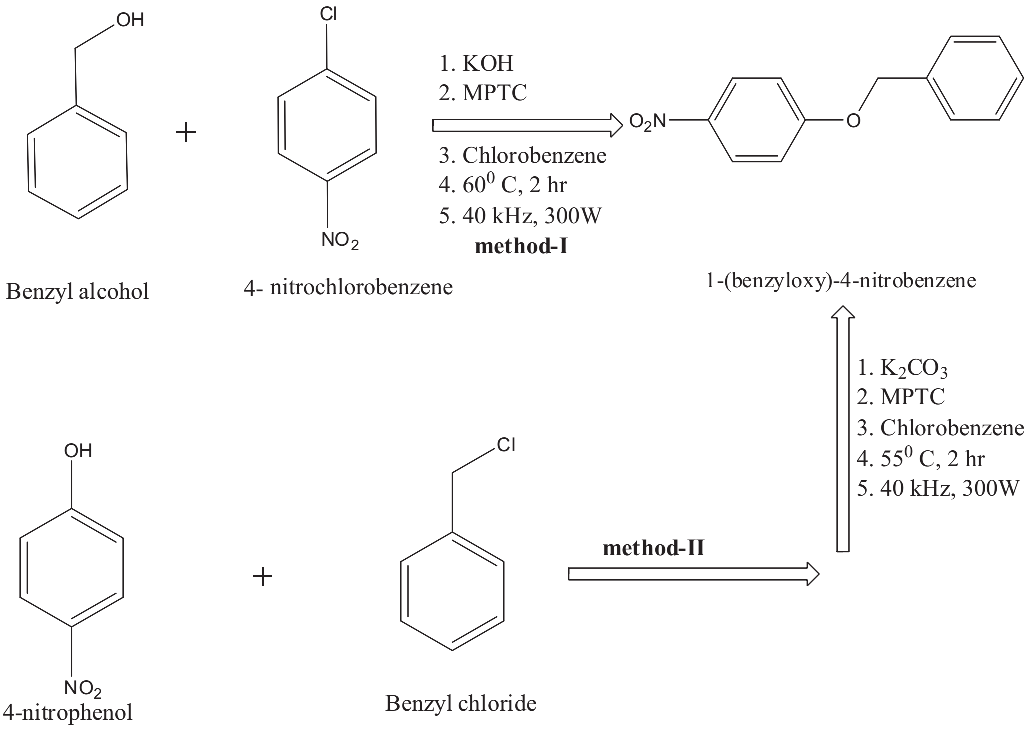
3.2. Method-II

To the well powdered K_2CO_3 (15 g) in 2 mL water, the 4-nitrophenol (1.7 g, 12.0 mmol) was added under overhead stirring for few minutes to generate the 4-nitrophenol anion. Then, benzyl chloride (1 g, 7.8 mmol) and the newly synthesized MPTC (0.2 g) in chlorobenzene (30 mL) were added slowly. The reaction mixture was heated at 55 °C for 2 h with vigorous stirring. The product formed was evidenced by Thin Layer Chromatography (TLC). The crude product was isolated by simple extraction with ethyl acetate (3 × 25 mL). The organic layer was collected and the solvent was evaporated under reduced pressure. The crude product was subjected to chromatography (SiO_2) employing hexane:ethyl acetate (9:1) as an eluent to obtain the product viz., (1-(benzyloxy)-4-nitrobenzene; Scheme 2) in the form of colorless solid. The identity of the product was confirmed by thin layer chromatography (TLC) and the melting point of the compound (1-(benzyloxy)-4-nitrobenzene) compared with authentic sample.

4. Reaction mechanism and kinetic model

The hydration of potassium salt of benzyl alcohol is serious. Therefore, only a small amount of product was obtained when the reaction is carried out in a liquid (water)–liquid (organic solvent) two-phase solution, even in the presence of quaternary ammonium salt. In this work, only a trace amount of water added to the reaction system in order to minimize the loss of reactant due to hydration. In general, the reaction of a solid reactant and organic substrate was verified by many scientists [1,8,24–26]. The reaction mechanisms of the solid–liquid phase-transfer catalysis can be classified as the non-soluble system (heterogeneous solubilization) and soluble system (homogeneous solubilization), which depend on the solubility of the inorganic salt of anion in the organic solvent. In this work, potassium salt of benzyl alcohol is soluble in organic solvent (chlorobenzene). The solid part of $PhCH_2O^-K^+$ is in equilibrium with its soluble part. Phase-transfer catalyst (MPTC) i.e., Q^+Cl^- would react with the soluble parts of $PhCH_2O^-K^+$ to form $PhCH_2O^-Q^+$ in the solid–liquid interface. Then the formed $PhCH_2O^-Q^+$ ion-pair transfers from the solid–liquid interface to the bulk organic phase where it reacts with 4-chloronitrobenzene (CNB) and produce the desired product (1-(benzyloxy)-4-nitrobenzene, Scheme 3).

The kinetic study of synthesizing 1-(benzyloxy)-4-nitrobenzene compound, the overall reaction of benzyl alcohol and 4-chloronitrobenzene (CNB) was catalyzed by the newly prepared MPTC (Q^+Cl^-) in the alkaline (KOH) bi-phase medium (Solid–Liquid) and is represented in Scheme 3. The reaction is carried out under MPTC assisted ultrasonic irradiation condition (40 kHz, 300 W) under pseudo first-order condition. In the current investigation the kinetics was followed in the presence of an excess amount of benzyl alcohol and by fixing 4-chloronitrobenzene (CNB) as limiting agent. The main reason for investigating this reaction is the



Scheme 2. Preparation of 1-(benzyloxy)-4-nitrobenzene.

effect of low frequency ultrasound irradiation (40 kHz, 300 W) along with agitation speed (300 rpm) to find out the effect of change of k_{app} value of this system.

4.1. Definition

The conversion (X) of 4-chloronitrobenzene (CNB) is defines as follows:

$$X = 1 - \{[\mathrm{CNB}]_0/[\mathrm{CNB}]_{0,t}\} \tag{1}$$

where $[\mathrm{CNB}]_0$ and $[\mathrm{CNB}]_{0,t}$ represent the concentration of 4-chloronitrobenzene in the organic phase at a given time (t) $t = 0$ and $t > 0$, respectively.

4.2. Rate expression

The rate expression for this reaction may be expressed as;

$$-r_{\mathrm{CNB}} = k_{app}[\mathrm{CNB}]_0 \tag{2}$$

where $[\mathrm{CNB}]_0$ is concentration of 4-chloronitrobenzene in the organic phase and k_{app} is the apparent reaction rate constant. This reaction is carried out in a batch reactor, so the diminution rate of CNB with time (t) can be expressed as

$$-d[\mathrm{CNB}]0/dt = -r_{\mathrm{CNB}} = k_{app}[\mathrm{CNB}]_{0,t} \tag{3}$$

On integrating the Eq. (3) yields:

$$-\ln(1 - X) = k_{app} * t \tag{4}$$

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

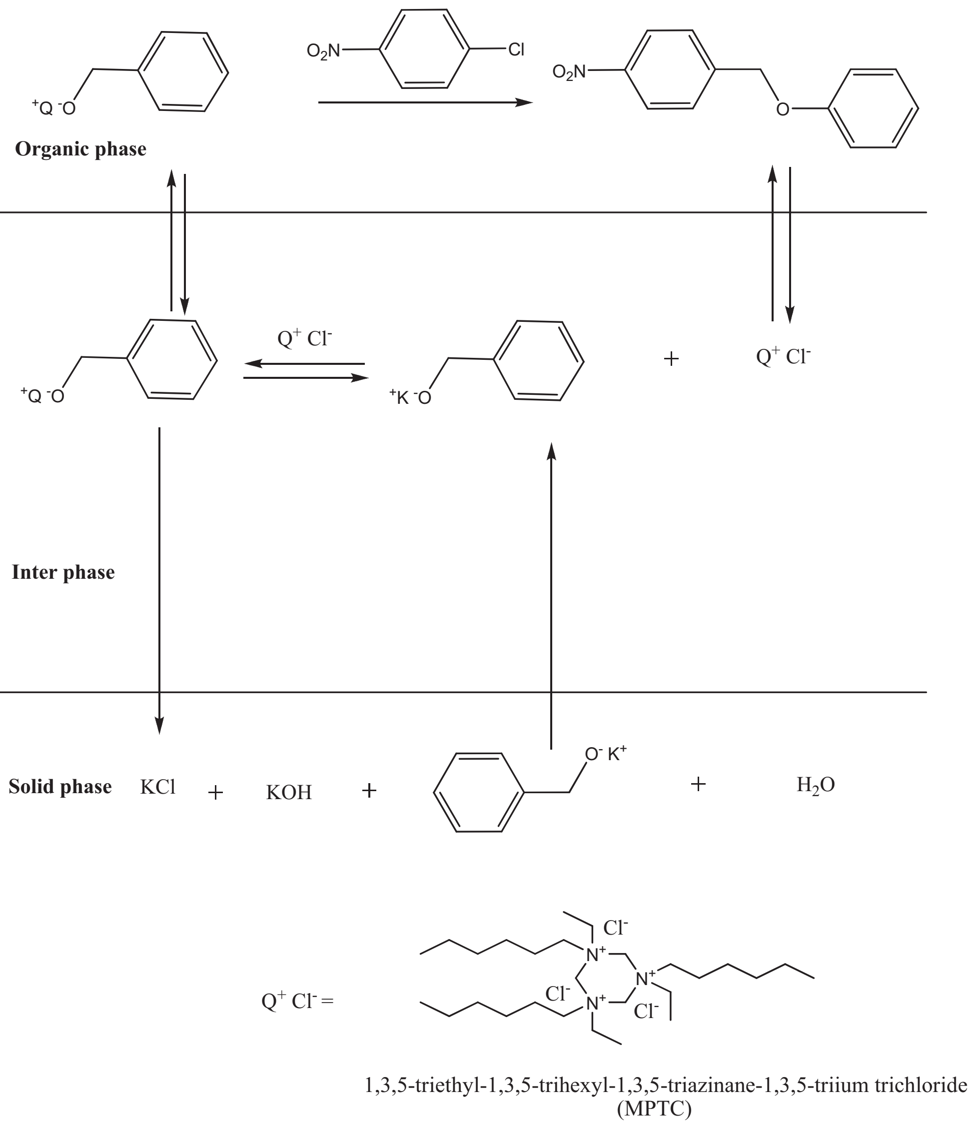
5. Results and discussion

The reaction was conducted in a 250 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 supported at the centre of the sonicator. Known quantities of chlorobenzene (30 mL, solvent), potassium hydroxide powder (10 g in 1 mL water) and 0.2 g biphenyl (IS-internal standard) were introduced into the reactor. Then, 1.0 g of benzyl alcohol (9.25 mmol) and 1 g of 4-chloronitrobenzene (6.35 mmol), 0.2 g of the newly synthesized MPTC were introduced to the reactor to start the reaction. The reaction mixture was stirred at 300 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 $CaCl_2$ was placed in the sample vials to absorb 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 4-chloronitrobenzene 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 °C; FID detector (300 °C). Yields were determined from standard curve using biphenyl as an internal standard.

5.1. Effects of ultrasound and mechanical stirring on the reaction

To ascertain the influence of agitation speed on the rate of O-arylation of benzyl alcohol, the speed of agitation was varied in the range of 0–500 rpm along with ultrasound irradiation (40 kHz, 300 W) using 1,3,5-triethyl-1,3,5-trihexyl-1,3,5-triazinane-1,3,5-triium trichloride (MPTC).

In principle, the homogeneous reaction is independent of the agitation speed. As shown in Table 1, that the rate of the reaction increases linearly as the agitation speeds increases from 0 to 300 rpm. Macroscopically, this result indicates that the reaction is carried out in a solid–liquid phase. In fact, the reaction proceeds by accompanying with the dissolving $PhCH_2O^-K^+$ in chlorobenzene. The dissolving rate of $PhCH_2O^-K^+$ in chlorobenzene is



Scheme 3. General mechanism.

highly influenced by the agitation speed. In general, a high concentration of $PhCH_2O^-K^+$ dissolving in organic solvent is obtained at a high agitation speed. Therefore, the conversion of 4-chloronitrobenzene was increased with the increase in the agitation speed up to 300 rpm. For agitation speeds higher than 300 rpm, the conversion is influenced almost not at all by the agitation speed. The purpose of stirring is to provide a well mixing to dissolve $PhCH_2O^-K^+$ in the chlorobenzene in the presence of MPTC to form $PhCH_2O^-Q^+$. Then, the dissolved $PhCH_2O^-Q^+$ reacted with 4-chloronitrobenzene to produce 1-(benzyloxy)-4-nitrobenzene. Therefore, the agitation speed was set at 300 rpm for studying the reaction phenomena from which the resistance of mass transfer stays at a constant value [27–35]. The k_{app} values 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 in solid–liquid systems, high erosion of the solid particles occurs and consequently the surface area is increased. So on, further when the same reaction was carried out in conventional method, the observed k_{app} value ($k_{app} = 6.2 \times 10^{-3}$, min^{-1}) almost four fold lesser than in the presence of ultrasonication (40 kHz, 300 W, 300 rpm: $k_{app} = 24.63 \times 10^{-3}$, min^{-1}).

Table 1
Effects of ultrasound and mechanical stirring speeds on the arylation of benzyl alcohol; 10 g of KOH, in 1 mL H_2O, 0.2 g of biphenyl (internal standard), 9.25 mmol of benzyl alcohol, 0.2 g of MPTC, 6.35 mmol of 4-chloronitrobenzene, 30 mL of chlorobenzene, 60 °C; ultrasound condition (40 kHz, 300 W).

Stirring speed (rpm) (40 KHz, 300 W)	$k_{app} \times 10^3$, min^{-1}
0	6.30
50	10.52
100	12.98
150	15.50
200	19.23
250	22.65
300	24.63
350	24.75
400	24.88
450	24.95
500	25.01

5.2. Effect of the amount of newly prepared MPTC

The experiments were conducted by varying the amount of the newly synthesized MPTC viz., 1,3,5-triethyl-1,3,5-trihexyl-1,3, 5-triazinane-1,3,5-triium trichloride by keeping other experimental parameters are kept constant. The influence of the amount of MPTC on the arylation of benzyl alcohol has been studied by varying amount of MPTC from 0.1 to 0.3 g with respect to 4-chloronitrobenzene (CNB) under ultrasound irradiation (40 kHz, 300 W). As shown in Fig. 1, the rate of conversion is increased with increasing in the amount of MPTC along with ultrasound irradiation (40 kHz, 300 W). The conversion about 75% in the higher concentration of multi-site phase-transfer catalyst in 30 min of the reaction. The increase in the k_{app} value is attributed to the synergic effect of ultrasound might be enlarged [36]. The small amount of water can efficiently promote the solubilization of the solid reactant and thus enhance the formation of catalytic intermediate ($PhCH_2O^-Q^+$). All the further experiments were done at 0.2 g of catalyst amount.

5.3. Effect of the concentration of 4-chloronitrobenzene

To investigate the influence of 4-chloronitrobenzene (CNB) on the kinetics of synthesis of 1-(benzyloxy)-4-nitrobenzene under ultrasonic irradiation condition (40 kHz, 300 W), the amount of CNB was varied from 0.6 to 1.4 g. The results are shown in Table 2. The data clearly indicates that the k_{app} value increases with increasing the amount of CNB. When the 4-chloronitrobenzene concentrations increased, the probability of finding the substrate with active-site of the catalyst and ultrasound enhanced the rate of the reaction [36,37]. It may be due to reduces the surface area between the solid and organic phases, and hence more reactants collide to each other simultaneously we get higher k_{app} value.

5.4. Effect of temperature

The effect of temperature on the reaction between benzyl alcohol and 4-chloronitrobenzene was studied under otherwise similar conditions. The temperature was varied from 40 to 80 °C (Fig. 2).

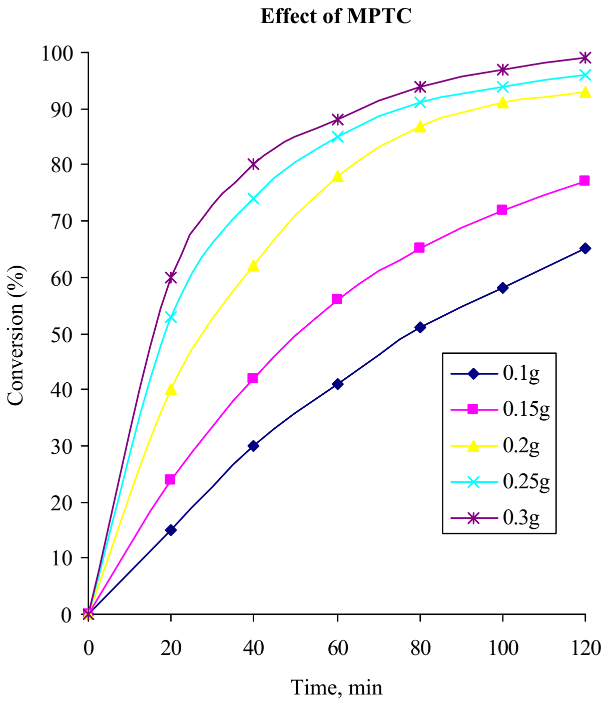


Fig. 1. Effect of the amount of MPTC on the apparent rate constant: 10 g of KOH, in 1 mL H_2O, 0.2 g of biphenyl (internal standard), 9.25 mmol of benzyl alcohol, 6.35 mmol of 4-chloronitrobenzene, 30 mL of chlorobenzene, 300 rpm, 60 °C; ultrasound condition (40 kHz, 300 W).

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 [38]. 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 [39,40]. 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. 6 of $-\ln k_{app}$ against $1/T$ to get activation energy of 53.32 kJ mol^{-1}. From the literature survey, the dehydrobromination of (2-bromoethyl) benzene catalyzed by tetraoctylammonium bromide (TOAB), an extraction mechanism was proposed [41] due to lower E_a value (<43 kJ mol^{-1}). In general, higher activation energy (more than 43 kJ mol^{-1}) suggests an interfacial mechanism [37,42]. 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 [43]. Further, in the N-alkylation of pyrroleidine-2-one, the E_a (51.35 kJ mol^{-1}) was reported by Sasson and Bilman [44] and for this reaction they proposed an interfacial mechanism. They concluded that the deprotonation of the substrate takes place at the inter-phase and consequently the organic anion is extracted and reacts in the bulk organic phase. The rate-determining step in the process is the anion exchange at the inter-phase. In our study, the observed E_a value is 53.32 kJ mol^{-1} (64.66 kJ mol^{-1} under silent condition). Hence, we proposed an interfacial mechanism for our present study [37,45,46].

5.5. Effect of ultrasonic power

Ultrasonic irradiation is defines as acoustic waves with frequencies in the 20 kHz–100 MHz range [47]. They create cavities generating locally high temperature and pressures [48–51] or strong electric fields [49,51–53]. 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 cavitations [50]. It has been reported that a combination of PTC and ultrasound is often better than either of the two techniques alone [51]. 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 arylation of benzyl alcohol with same output power of 300 W, the ultrasonic frequency was varied between 28 and 40 kHz under otherwise similar conditions using MPTC as the catalyst and also we followed the reaction under silent condition (0 kHz). The kinetic profile of the reaction is obtained by plotting $-\ln(1 - X)$ against time. In our experimental condition at 30 min, without ultrasonic irradiation (silent condition) the k_{app} values is 6.20×10^{-3}, min^{-1} but in the presence of ultrasonic condition the k_{app} values are 17.51×10^{-3}, min^{-1} and 24.63×10^{-3}, min^{-1}

Table 2
Effect of amount of 4-chloronitrobenzene (CNB) on the rate of arylation of benzyl alcohol under ultrasonic condition: 10 g of KOH, in 1 mL H_2O, 0.2 g of biphenyl (internal standard), 9.25 mmol of benzyl alcohol, 0.2 g of MPTC, 30 mL of chlorobenzene, 300 rpm, 60 °C; ultrasound condition (40 kHz, 300 W).

4-Chloronitrobenzene (CNB) (g)	$k_{app} \times 10^3$, min^{-1} (40 kHz, 300 W)
0.6	13.23
0.8	19.52
1	24.58
1.2	28.30
1.4	31.78

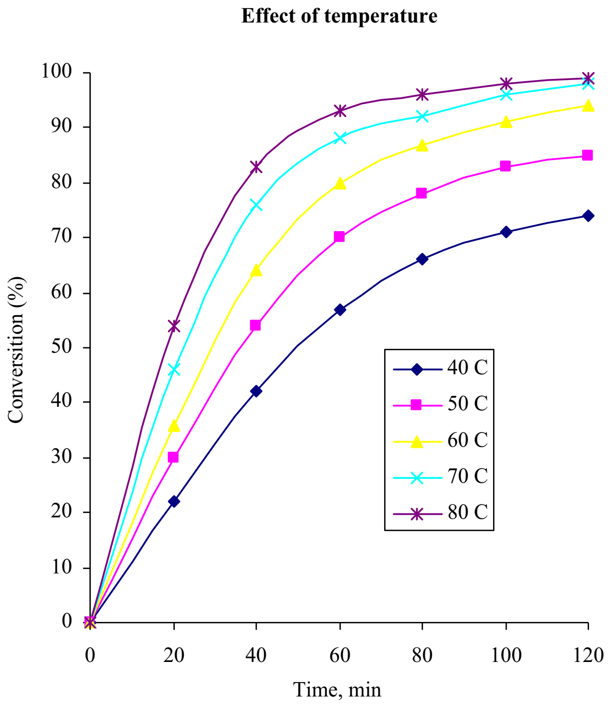


Fig. 2. Effect of temperature on the apparent rate constant: 10 g of KOH in 1 mL H_2O, 0.2 g of biphenyl (internal standard), 9.25 mmol of benzyl alcohol, 6.35 mmol of 4-chloronitrobenzene, 0.2 g of MPTC, 30 mL of chlorobenzene, 300 rpm, and ultrasound condition (40 kHz, 300 W).

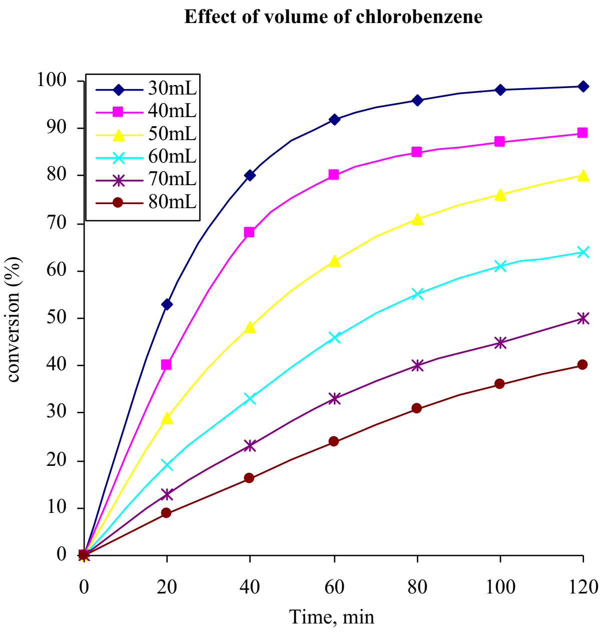


Fig. 3. Effect of volume of chlorobenzene on the apparent rate constant: 10 g of KOH in 1 mL H_2O, 0.2 g of biphenyl (internal standard), 9.25 mmol of benzyl alcohol, 6.35 mmol of 4-chloronitrobenzene, 0.2 g of MPTC, 60 °C, 300 rpm, ultrasound condition (40 kHz, 300 W).

for 28 kHz (300 W) and 40 kHz (300 W), respectively (Table 3). Hence, the overall k_{app} was increased by increasing the ultrasonic frequency in the order of 0 kHz (silent condition) <28 kHz (300 W) <40 kHz (300 W) for our system (Table 3) .Similar trend was observed by Entezari et al. [54,55].

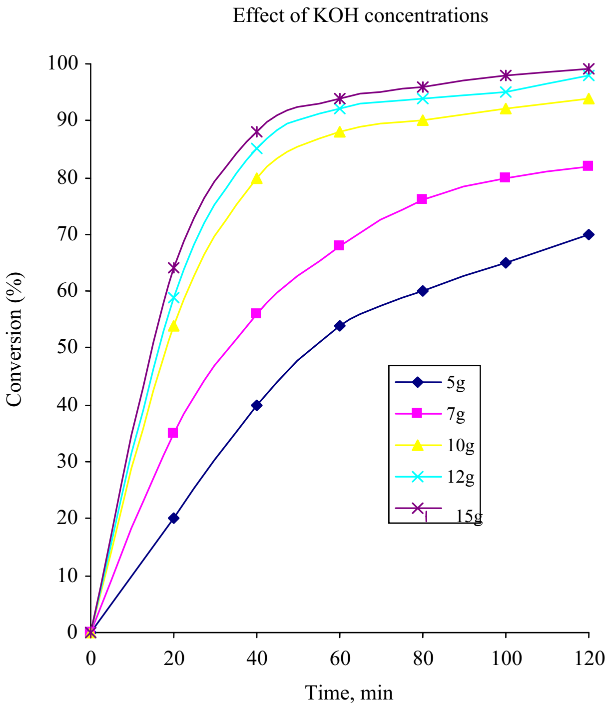


Fig. 4. Effect of KOH concentrations on the apparent rate constant: 0.2 g of biphenyl (internal standard), 9.25 mmol of benzyl alcohol, 0.2 g of MPTC, 6.35 mmol of 4-chloronitrobenzene, 30 mL of chlorobenzene, 60 °C, 300 rpm, ultrasound condition (40 kHz, 300 W).

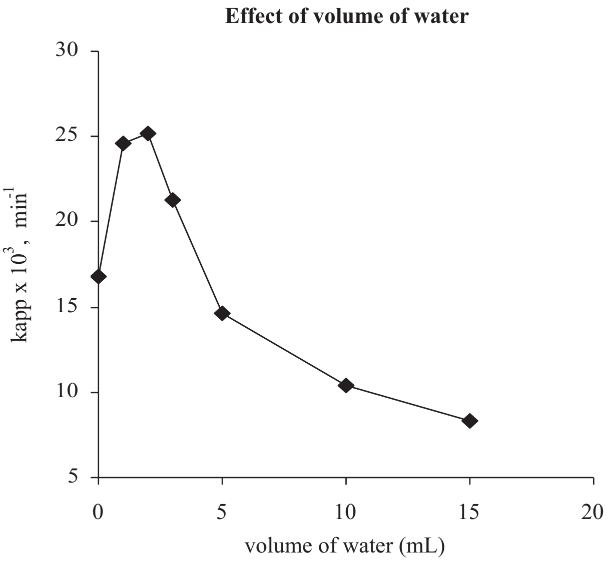


Fig. 5. Effect of the volume of water on the apparent rate constant: 10 g of KOH, 0.2 g of biphenyl (internal standard), 9.25 mmol of benzyl alcohol, 6.35 mmol of 4-chloronitrobenzene, 0.2 g of MPTC, 30 mL of chlorobenzene, 300 rpm, 60 °C; ultrasound condition (40 kHz, 300 W).

5.6. Effect of organic solvents

The influence of various organic solvents on the rate of arylation of benzyl alcohol was followed under otherwise standard reaction conditions. Five organic solvents employed in this study are toluene, anisole, cyclohexane, chlorobenzene, and n-hexane. From the plot of $-\ln(1-X)$ against time, the k_{app} values are obtained. From the Table 4, chlorobenzene possesses a higher k_{app} value among the five organic solvents, due to its higher dielectric

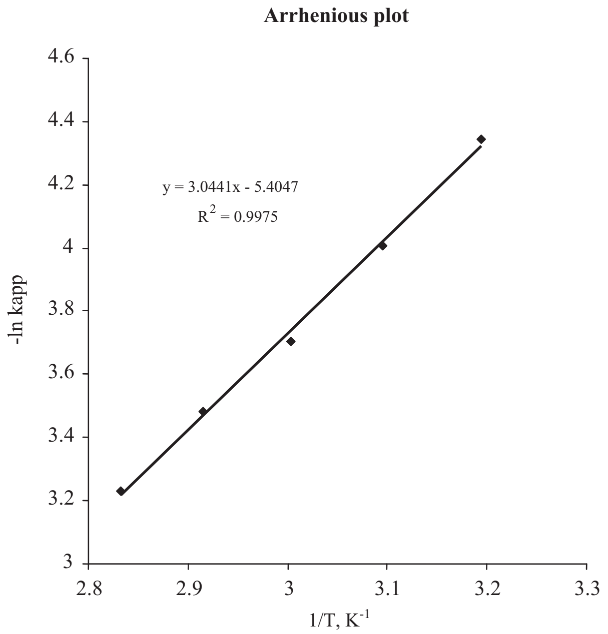


Fig. 6. Arrhenius plot; 10 g of KOH in 1 mL H_2O, 0.2 g of biphenyl (internal standard), 9.25 mmol of benzyl alcohol, 6.35 mmol of 4-chloronitrobenzene, 0.2 g of MPTC, 30 mL of chlorobenzene, 60 °C, 300 rpm, ultrasound condition (40 kHz, 300 W).

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 [56].

5.7. Effect of volume of chlorobenzene

In a homogeneous reaction, the reaction follows the intrinsic kinetic law. The conversion or the reaction rate is directly proportional to the concentration of the reactants in 30 min of reaction. A dilute concentration of the reactant is obtained using a large amount of organic solvent. The conversion of 4-chloronitrobenzene is increased with the decrease in the volume of chlorobenzene. Fig. 3 shows the dependence of the% conversion on the volume of chlorobenzene. The k_{app} value is inversely proportional to the volume of chlorobenzene, as expected.

5.8. Effect of different phase-transfer catalysts

Comprehensive comparative kinetic studies for the arylation of benzyl alcohol by 4-chloronitrobenzene (CNB) were carried out using 5 mol% of various onium salts viz., 1,3,5-triethyl-1,3,5-trihexyl-1,3,5-triazinane-1,3,5-triium trichloride (MPTC), tetraethylammonium chloride (TEAC), tetraethylammonium bromide (TEAB), tetrabutylammoniun chloride (TBAC), tetrabutylammonium bromide (TBAB), benzyltriethylammonium chloride (BTEAC), and benzyltriethylammonium bromide (BTEAB). The pseudo-first order rate constant are evaluated for all the catalyst from the plot of $-\ln(1-X)$ versus time and are presented in Table 5, with ultrasonic condition. The order of the relativities of these quaternary ammonium salts are in the order MPTC > TBAB > TBAC > BTEAC > TEAB > TEAC. It is thus concluded that the order of the reactivity is TEA cation > BTEA cation > TBA cation, which is consistent with the result [42] obtained by Wang and Rajendran combined with ultrasonic dichlorocarbene addition to 1, 7-octadiene under PTC condition. The results indicates that the k_{app} value depends on organophilisity of the onium salts along with ultrasonic irradiation condition (Table 5) [36].

Table 3
Influence of ultrasonic frequencies on the rate of arylation of benzyl alcohol: 10 g of KOH, in 1 mL H_2O, 0.2 g of biphenyl (internal standard), 9.25 mmol of benzyl alcohol, 0.2 g of MPTC, 6.35 mmol of 4-chloronitrobenzene, 30 mL of chlorobenzene, 300 rpm, 60 °C.

Ultrasonic frequency (kHz)	$k_{app} \times 10^3$, min^{-1}
0	6.20
28	17.51
40	24.62

Table 4
Influence of organic solvents on the rate of O-arylation of benzyl alcohol under ultrasonic condition: 15 g of KOH, in 1 mL H_2O, 0.2 g of biphenyl (internal standard), 9.25 mmol of benzyl alcohol, 0.2 g of MPTC, 6.35 mmol of 4-chloronitrobenzene, 30 mL of chlorobenzene, 300 rpm, 60 °C; ultrasound condition (40 kHz, 300 W).

Solvents	Dielectric constant (ε^a)	$k_{app} \times 10^3$, min^{-1} (40 kHz, 300 W)
Chlorobenzene	5.6	24.6
Anisole	4.3	21.8
Toluene	2.4	15.4
Hexane	2.2	11.5
Cyclohexane	2.0	9.6

5.9. Effect of various potassium hydroxide concentrations

In the PTC/base catalyzed reactions, the reaction rate is known to be greatly affected by a concentration of the alkaline compound. The rate of arylation of benzyl alcohol strongly depends on the strength of the potassium hydroxide. Kinetic experiments were carried out, by employing 5–20 g of KOH (1 mL water) under otherwise similar reaction conditions. The kinetic profile of the reaction is obtained by k_{app} against amount of KOH. The k_{app} values tremendously increased with increasing in basicity of OH^- ion and after 15 g stay almost constant (Fig. 4). It suggest that the hydroxide ions which are less solvated by water molecules at higher amount of KOH and there by the k_{app} value increases [42,44].

5.10. Effect of water

The critical effect of traces of water on solid–liquid phase transfer reactions has been studied in detail by several groups [4,57–59].

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 under 300 rpm and ultrasonic irradiation (40 kHz 300 W). Fig. 5 is the plot of conversion versus volume of water (mL) for different amounts of water added, showing that pseudo-first-order kinetic equation can be successfully used to describe the ultrasound assisted-SLPTC system. Without adding water, only

Table 5
Effect of various PTC's (0.3 g based on the limiting reagent, 4-chloronitrobenzene) on the rate of arylation of benzyl alcohol under ultrasonic condition: 10 g of KOH, in 1 mL H_2O, 0.2 g of biphenyl (internal standard), 9.25 mmol of benzyl alcohol, 6.35 mmol of 4-chloronitrobenzene, 30 mL of chlorobenzene, 300 rpm, 60 °C; ultrasound condition (40 kHz, 300 W).

PTC (g)	$k_{app} \times 10^3$, min^{-1} (40 kHz, 300 W)
MPTC	24.6
TEAC	17.2
TEAB	16.4
BTEAC	15.6
BTEAB	14.3
TBAB	13.5

47% of product yield was obtained in 60 min of reaction; but merely with 1 mL of water in the system, the product yield largely increased to 85.3%. Continuing to increase the quantity of water, the reaction rate was increased for further 1 mL and then gradually reduced. When the amount of water was added to 15 mL, the solid–liquid system became a liquid–liquid type, and the product yield greatly decreased to 30%, 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 $PhCH_2O^-Q^+$ in the inter-phase, thus enhancing the intrinsic reaction rate. When more water was added, the effective concentration of $PhCH_2O^-Q^+$ in the inter-phase would be decreased and the reaction rate was reduced. In the absence of water, the reaction rate of solid reactant and MPTC in the organic phase was slow, resulting in small product yield 49% after 30 min of reaction. With only 1 mL of water, the formation of $PhCH_2O^-Q^+$ greatly increased and concentrated in the inter-phase and leads to the bulk organic phase where the intrinsic reaction take place.

6. Discussion of the reaction between 4-nitrophenol and benzyl chloride

Known quantities of multi-site phase transfer catalyst (MPTC) viz., viz., 1,3,5-triethyl-1,3,5-tri hexyl-1,3,5-triazinane-1,3,5-triium trichloride (0.2 g), benzyl chloride (1 g, 7.8 mmol) and 0.2 g biphenyl (internal standard in the analysis) in chlorobenzene solvent (30 mL) were added slowly to the mixture of well powdered potassium carbonate (15 g) in 2 mL water, 4-nitrophenol (1.7 g, 12.0 mmol), and agitated (300 rpm) in a 250 mL three-necked Pyrex round – bottom batch reactor, which was immersed in a constant – temperature (55 °C) ultrasonicator (40 kHz, 300 W). During the reaction, 0.2 mL of the organic sample was withdrawn at the chosen time and diluted into 3 mL of chlorobenzene. The samples analyzed by a gas chromatography (GC – Varian 3700 model). The product viz., (1-(benzyloxy)-4-nitrobenzene) was determined from standard curve using biphenyl as an internal standard. In the present solid–liquid system, the mechanism is illustrated by the reaction of organic substrate (benzyl chloride, BzCl) with the active intermediate $NO_2–C_6H_4–OQ$. Without an extra addition of water, the multi-site phase transfer catalyst (QX) diffuses to the surface of the solid particles of $NO_2–C_6H_4–OK$ and converts it into the form of $NO_2–C_6H_4–OQ$, which then dissolves in the bulk organic phase.

For the reaction of solid reactant $NO_2–C_6H_4–OK$ and organic substrate, benzyl chloride (BzCl) catalyzed by the multi-site phase transfer catalyst (QX), the overall reaction is:

$$NO_2 - C_6H_4 - OK\ (S) + BzCl\ (org) \xrightarrow{QX} NO_2 - C_6H_4 - OBz\ (org) + KCl\ (S) \tag{1}$$

where (S) indicates the solid phase.

The following steps are contained in the overall reaction:

(i) Reaction of $NO_2–C_6H_4–OK$ with QX produce $NO_2–C_6H_4–OQ$ at near the solid–liquid interface. This reaction is usually reversible and fast compared with the intrinsic organic reaction. This reaction is written as:

$$NO_2 - C_6H_4 - OK + QX \leftrightarrow NO_2 - C_6H_4 - OQ\ (org) + KX\ (org) \tag{2}$$

(i) Equilibration of KX

The product KX (org) is also in equilibrium with its solid parts and is limited by the solubility in the organic phase:

$$KX\ (org) \leftrightarrow KX\ (S) \tag{3}$$

(i) Reaction of $NO_2–C_6H_4–OQ$ with benzyl chloride, BzCl to form the desired product viz., 1-(benzyloxy)-4-nitrobenzene, $(NO_2–C_6H_4–OBz)$ which is represented in the Eq. (4).

$$NO_2 - C_6H_4 - OQ\ (org) + BzCl\ (org) \rightarrow NO_2 - C_6H_4 - OBz\ (org) + QCl\ (S) \tag{4}$$

7. Conclusion

In the present study, the rate of the reaction was controlled to study the kinetic aspects of the formation of the 1-(benzyloxy)-4-nitrobenzene from benzyl alcohol and 4-chloronitrobenzene (CNB) 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. 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], [KOH], ultrasonic frequency, stirring speed 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. 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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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ultsonch.2014.04.010.

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