Kinetic study of synergistic effect of multi-site phase transfer catalysis and ultrasound irradiation for the synthesis of 1, 3-bis (4-nitrophenoxy) benzene

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Phase transfer catalysis along with ultrasound technique proved to be useful in various organic heterogeneous reactions and recognized as a viable environmentally friendly. The influence of ultrasonic irradiation associated with a new multi site phase transfer catalyst (MPTC) on the synthesis of 1,3-bis(4-nitro phenoxy)benzene from 1,3-dihydroxy benzene with 1-chloro-4-nitrobenzene (CNB) under heterogeneous solid-liquid condition using sodium hydroxide as a base at 75^0C has been studied. The higher conversion of 1-chloro-4-nitrobenzene has been achieved by using the synergistic condition of ultrasonic irradiation (40 kHz, 300W) and multi-site phase transfer catalyst in better efficacy. The reaction rate enhance by decrease the volume of water. The apparent the reaction rate was found to be pseudo-first order kinetics. The apparent rate constant was increased linearly with the increase in the concentration of various parameters multi-site phase transfer catalyst, sodium hydroxide ultrasonic effect, stirring speed and temperature from Arrhenius plot the apparent activation energy (Ea) was also calculated.

Keywords: 1-Chloro-4-nitrobenzene, Interfacial reaction, MPTC, Ultrasound irradiation

The phase transfer catalyst acts to exact them from the aqueous phase and it moves anion to the organic phase that include as a part of reactant. Accordingly, there is a reaction between moved reagent and ion pair with the non convertible reactant in the organic phase. The phase-transfer catalysis (PTC) brings the reactants together and reacts in two mutually insoluble phases. It was widely used various industrial application. By using chemical reactions such as oxidations, reductions, polymerizations, transition metal co-catalyzed reactions, addition and condensations reactions so on[1-4]. Phase transfer catalyst it can be divided into two types i.e., liquid–liquid two phase PTC (LL-PTC)[5-7] and solid–liquid two phase PTC (SL-PTC)[8,9]. In the case of SL-PTC without using of water, the reaction rate is very elevated, almost insignificant by-products; embrace high in yields of products. The most widely used catalyst is Quaternary ammonium salts. Theory of multi-sited phase transfer catalyst (MPTC) (QX_2) was proposed by Idoux *et al*. by this reaction they have synthesized phosphonium and quaternary onium ions incorporating more than one active site per molecule[10]. The catalytic character of multi-site phase-transfer

catalysts got much attention, due to multiple molecules of the aqueous reactant can be passed into the reaction catalytic effect is thus augmented[11,12]. In comparison PTC has certain advantages, such as no needs for costly aprotic solvent, plain work-up, less reaction time and lower reaction temperature. This technique is limited using for more reactions. The reaction rates are more enhanced by using this method such as development of new catalyst along with ultrasound and microwave condition.

The use of ultrasound the phase transfer reaction can give higher yield of conversion that has higher rate of reaction due to the local increase in the temperature, this leads to generate of free radical with powerful turbulence. The ultrasound can raise the effectiveness of the phase transfer catalyst that give, an increases rate of the reaction and selection this method can never change its use. Ultrasonic cavitations generate a locally high temperature and pressure, as well as heating and cooling rates for chemical reaction[13-15]. In solid-liquid biphasic system under ultrasonic irradiation the interphase was disrupted by cavitational collapse and impels liquid jet into other forms droplets and leads to enhancement

of the reaction rate. The overall reaction rate can be effectively increased in the case of MPTC. Ultrasonic effect combined with SL-PTC has significant improvement in the reaction rate. However combinations of ultrasound in organic reactions have been reported. In this work we synthesized the multi-site phase-transfer catalyst (MPTC) viz., 1,1,4,4-tetramethylpiperazine-1,4-diium dichloride (Scheme 1) and used as a superior catalyst for the synthesis of 1,3-bis(4-nitrophenoxy)benzene from sodium salt of 1,3-dihydroxybenzene with 1-chloro-4-nitrobenzene (CNB) under heterogeneous solid–liquid condition. The kinetic study of arylation 1,3-dihydroxybenzene of using 1-chloro-4-nitrobenzene under controlled MPTC reaction conditions will be interesting, by the use of synthesized MPTC under ultrasonic irradiation condition (40 kHz; 300W), the kinetic study has been followed.

Experimental Section

Materials

All the reagents, including, 1,3-dihydroxy benzene, 1-chloro-4-nitrobenzene, N^1,N^1,N^2,N^2-tetramethylethane-1,2-diamine (Aldrich), 1,2-dichloroethane (Merck) biphenyl, tetrabutylammonium bromide (TBAB), tetrabutylammonium chloride (TBAC), tetrabutylammonium iodide (TBAI), tetrahexylammonium bromide (THAB), tetraoctylammonium bromide (TOAB), sodium hydroxide, ethylacetate, toluene, chlorobenzene, benzene, ethanol, diethyl ether and other reagents for synthesis were of guaranteed grade (GR) chemicals and were used without further purification.

Instrumentation

^{1}H NMR and ^{13}C spectra were recorded on a Bruker 300 MHz and 75 MHz respectively 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. The details of ultrasonic process equipment have been vividly explained in our previous report[16]. Figure 1 represents the schematic diagram of the experimental setup. The instrument was assembled with the two frequency 28 kHz/40kHz and with electric power of 300W and ultrasonic transducer
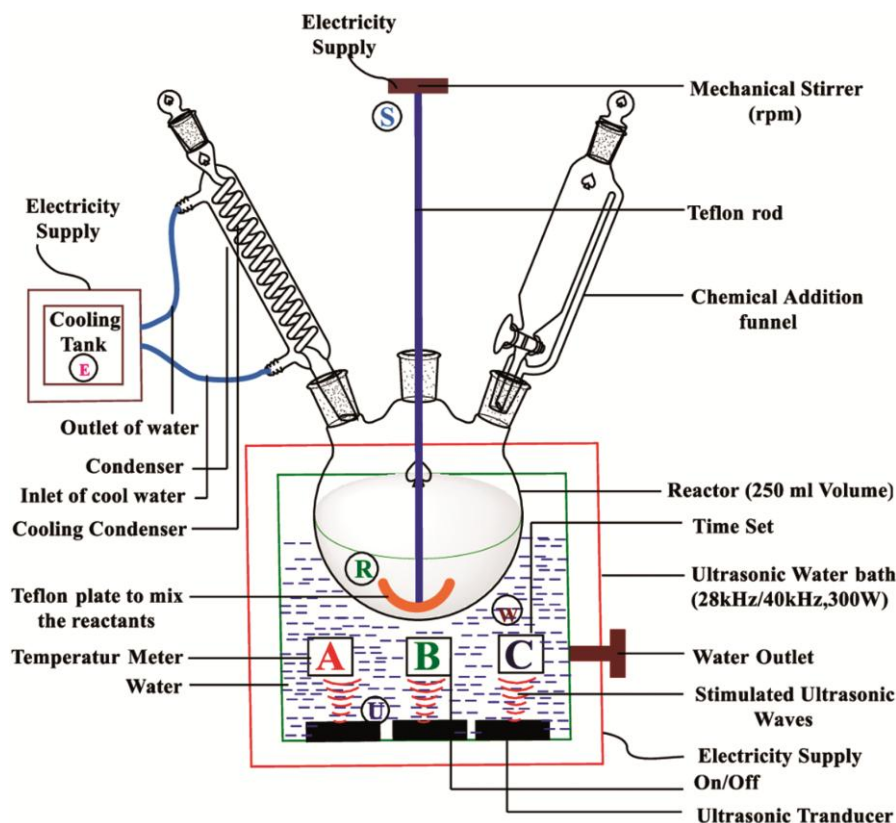

Fig. 1 — Schematic diagram of the experimental setup

head (U) produces the stimulated ultrasonic waves. (Figure 1) shows schematic diagram of experimental setup, where square shaped water bath capacity (W) 12 liters, it is incorporated with an ultrasonic water bath, with temperature control meter (A), time set (C), and on/off (B) respectively. This ultrasound water bath has an electric output of 300W and if the ultrasound machine fixed with a mechanical stirrer (S) in to the reactor (R), the reactor is 250 mL Pyrex glass flask. In the reaction it is suspended at the certain of ultrasonic cleaning bath to get the maximum radiation where the bottom of reactor is suspended in to the water level. The reactor is connected to an external cooling circulator tank (E) via, a cooling condenser. It is also connected with thermometer or dropping funnel. The ultrasound water tank (W) external cooling circulator (E) mechanical stirrer (S) connected with electric supply. The continuous ultrasound radiation through the water tank will produce high energy water waves for the molecules to collide with each other in reaction that leads to form the exacted product. So that pseudo first order condition is applied.

### Synthesis of a new multi-site phase-transfer catalyst (MPTC)

A mixture of N^1, N^1, N^2, N^2-tetramethylethane-1,2-diamine (21.51 mmol), 1,2-dichloroethane (17.13 mmol) and 80 mL of ethanol was placed in a 250 mL three necked round bottomed Pyrex flask. The reaction was carried out at 60°C for 24h and was gently refluxed in the nitrogen atmosphere. The solvent was

then completely removed under vacuum and onium salt, i.e., 1,1,4,4-tetramethylpiperazine-1,4-diium dichloride, (MPTC; Scheme 1) was washed with n-hexane (4×25 mL). The Colourless solid was stored in CaCl$_2$ desiccator. Yield: 94%; ^{1}H NMR (500 MHz, DMSO); δ 3.35 (s, 12H, N^+ –CH$_3$), δ 3.86(s, 8H, N^+ –CH$_2$), ^{13}C NMR (125 MHz, DMSO): δ 55.499(N^+ –CH$_3$), δ 61.466 (N^+ –CH$_2$)

Elemental analysis: Calculated: C, 31.60%; H, 6.63%; Br, 52.56%; N, 9.21%; and Found: C, 31.08%; H, 6.59%; Br, 32.50%; N, 9.11%.

Synthesis of 1, 3-bis (4-nitrophenoxy) benzene

To the well powdered NaOH (10g) in 2mL water and the 1, 3-dihydroxybenzene (45.41mmol) was added under overhead stirring for few minutes to generate the 1,3-dihydroxybenzene anion. Then 1-chloro-4-nitrobenzene (20.31mmol) and the newly synthesized MPTC (3 mol %) in chlorobenzene (30mL) were added slowly. The reaction mixture was heated at 75°C for 2 hours 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 x 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 (9.7:0.3) as an eluent to obtain a pure derivative (1, 3-bis (4-nitrophenoxy)benzene; Scheme 2) in the form of
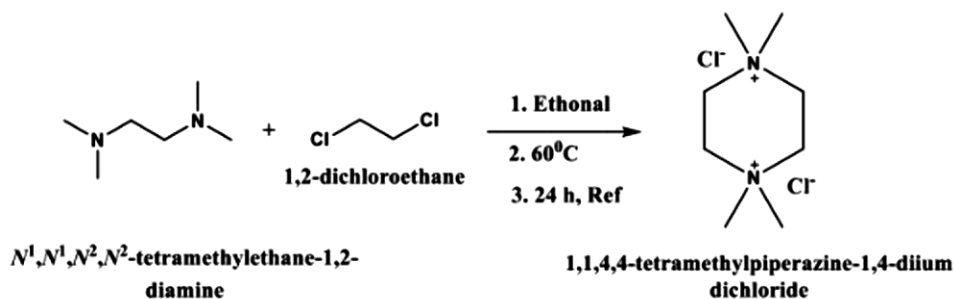
Scheme 1 — Synthesis of 1,1,4,4-tetramethylpiperazine-1,4-diium dichloride (MPTC)
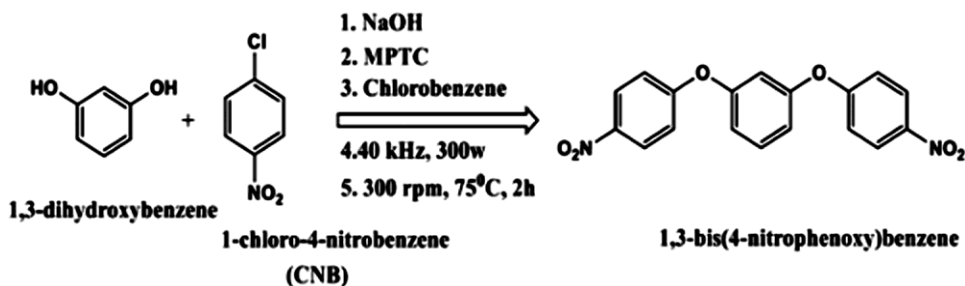
Scheme 2 — Preparation of 1,3-bis(4-nitrophenoxy)benzene

brownish 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 (1,3-bis(4-nitrophenoxy)benzene) is 150-152°C; ^{1}H NMR (300 MHz, CDCl₃): δ 6.224(s,1H, 1,3-dihydroxybenzene-H), 6.909-6.939 (d, 1H, 1,3-dihydroxybenzene-H), 7.133 - 7.162 (d, 2H, 1,3-dihydroxybenzene-H), 7.337-7.366 (d, 2H, 1-chloro-4-nitrobenzene-H) 8.117-8.148(d, 2H, 1-chloro-4-nitrobenzene-H-near NO₂ group); ^{13}C NMR (75 MHz, CDCl₃): δ. 103.76, 113.94, 129.82, 157.46 (1,3-dihydroxybenzene-C). 117.71, 123.10, 141.76, 163.60 (4-chloronitrobenzene-C).

Elemental analysis; Calculated: C, 61.40%; H, 3.45%; N, 7.98%; O, 27.27% and Found: C, 61.37%; H, 3.43%; N, 7.95%; O, 27.25% .
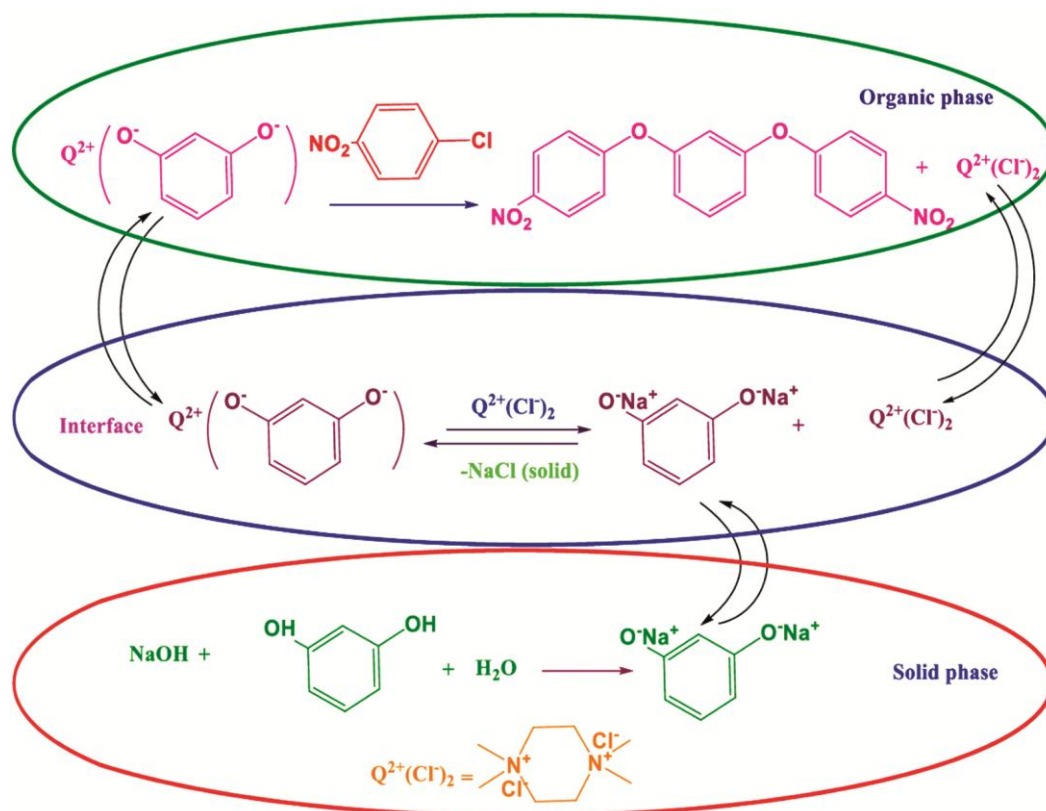
Reaction mechanism

The hydration of sodium salt of 1,3-dihydroxybenzene is serious. Therefore, only a small amount of product was obtained when the reaction was 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 was added to the reaction system in order to minimize the loss of reactant due to hydration. The reaction of a solid reactant and organic substrate was verified by many researchers[17-20]. 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, sodium salt of 1,3-dihydroxybenzene is sparingly soluble in organic solvent (chlorobenzene). First, sodium salt of 1,3-dihydroxybenzene was dissolved in the organic solvent with the addition of quaternary ammonium salt, i.e. Ph(O⁻Na⁺)₂ dissolving in the organic solvent reacts with quaternary ammonium salt to form an active intermediate[Q²⁺(Ph(O⁻)₂)]. The inorganic salt NaX precipitated as a solid form in the organic solution. The active $Q^{2+}(Ph(O^-)_2)$ (org) then reacted with 1-chloro-4-nitrobenzene (CNB) to produce the desired product (1,3-bis(4-nitrophenoxy)benzene, (Scheme 3).

Kinetics of reaction

The reaction was conducted on a 250 mL three-necked Pyrex round-bottom flask. This permits agitating the solution, inserting the water condenser to

Scheme 3 — General mechanism

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), well powdered sodium hydroxide (10g in 2mL water) and 0.2 g biphenyl (IS-internal standard) were introduced into the reactor. Then, 5g of 1,3-dihydroxybenzene (45.41 mmol) and 3.2 g of 1-chloro-4-nitrobenzene (20.31 mmol), 3 mol% of the newly synthesized MPTC were introduced to the reactor to start the reaction. The reaction mixture was stirred at 300 rpm. The phase of separation was almost immediate on arresting the stirring process. Samples were collected from the organic layer at regular intervals. A pinch of anhydrous $CaCl_2$ was placed in the sample vials to absorb any moisture present in the organic layer and 0.5mL of chlorobenzene was added to the vials to dilute the solution. The kinetics was followed by estimating the amount of 1-chloro-4-nitrobenzene (limiting reagent) that disappeared and measured by a gas Chromatography (GC-Varian 3700 model). The analyzing conditions were as follows; Column, 30 m x 0.525 mm i.d. capillary column containing 100% poly(dimethyl siloxanen); injection temperature, 250°C; FID detector (300°C). Yields were determined by the standard curve using biphenyl as an internal standard.

Results and Discussion

Influence of stirring speed

To determine the influences of mass-transfer, the stirring speed was increased from 0 to 500 rpm along with ultrasound irradiation (40 kHz, 300W) using 1,1,4,4-tetramethylpiperazine-1,4-diium dichloride (MPTC). In principle, the heterogeneous reaction is dependent on the agitation speed. It can be seen from the (Table 1) that the dramatic increase in the reaction rate is produced with a raise in the stirring speed from 0 to 300 rpm. The possible reason is the interfacial area per unit volume of dispersion increases linearly as the agitation speeds increasing[21]. In fact, the reaction proceeds by dissolving $Ph(O^-Na^+)_2$ in chlorobenzene. The dissolving rate of $Ph(O^-Na^+)_2$ in chlorobenzene is highly influenced by the agitation speed. In general, a high concentration of $Ph(O^-Na^+)_2$ dissolving in organic solvent is obtained at a high agitation speed. Therefore, the conversion of 1-chloro-4-nitrobenzene was increased with the increase in the agitation speed up to 300 rpm. For agitation speed higher than 300 rpm, the conversion is not at all influenced by the agitation

Table 1 — Influence of Stirring speed	
Stirring speed (rpm)	k_{app} x 10^{-3}, min^{-1}
0	5.21
100	12.36
200	18.43
300	21.18
400	21.96
500	22.17

Reaction conditions: 10g of NaOH, in 2mL H_2O, 0.2g of biphenyl (internal standard), 45.41 mmol of 1,3-dihydroxybenzene, 20.3mmol of 1-chloro-4-nitrobenzene, 3mol% of MPTC, 30mL of chlorobenzene, 75^0C, ultrasound condition (40 kHz, 300W).

speed. This verifies that the reaction of $Ph(O^-Na^+)_2$ and 1-chloro-4-nitrobenzene was carried out in a homogeneous solution, i.e. $Ph(O^-Na^+)_2$ first dissolves gradually in chlorobenzene in the presence of MPTC to form $Q^{2+}(Ph(O^-)_2)$ at the inter-phase. Then, the formed intermediate $Q^{2+}(Ph(O^-)_2)$ reacted with 1-chloro-4-nitrobenzene to produce 1,3-bis(4-nitrophenoxy)benzene in the organic phase. Therefore, the agitation speed was set at 500 rpm for studying the reaction phenomena from which the resistance of mass-transfer stays at a constant value. When the reaction was carried out in conventional method, the observed k_{app} value (k_{app} = 6.48 × 10^{-3}, min^{-1}) was almost four fold lesser than in the presence of sonication (40 kHz, 300W) and stirring (k_{app} = 21.18 × 10^{-3}, min^{-1}). It is clear from (Table 1) that the k_{app} value for the sonication only (without stirring, 0 rpm) is 5.21 x 10^{-3}, min^{-1}. The k_{app} values indicate that the mechanical effects brought out by the use of low frequency ultrasounds are responsible for the enhancement of the kinetics by harsh mixing, enhancement of mass transfer, especially in solid-liquid systems, high erosion of the solid particles occur and the surface area between the two phases is decreased. Ultrasound decreases the surface area between the two layers [22].

Influence of Ultrasonic Power

Sonication was found to increase the rate of the reaction of solid–liquid phase-transfer catalysts (SL-PTC). Ultrasound influences intense local conditions generated through cavitation bubble dynamics such as the, disappearance, formation and nucleation and of vapour or gas bubbles in its field[23]. In this reaction, the enhancement of mass transfer is mainly due to the supporting mechanical effects i.e., agitation and ultrasound. The presence of ultrasound in SL-PTC system results the cavitational collapse near the solid–liquid interface that disrupts the interface and impels conversion of one reactive mass

into the other, forming fine emulsion thereafter proceeds to a dramatic enhancement in the interfacial contact area. In recent time few works are reported that multi-site phase-transfer catalyst (MPTC) combined with ultrasound shows the highest potential to increase the rate of the reaction or conversion[24].

To study the effect of ultrasound frequency, two different ultrasonic frequencies (28 kHz, 40 kHz) were used, having the same output power of 300W. The reaction is also carried out without ultrasound (conventional method). The mass-transfer resistant plays an important role in interfacial reaction, although the use of ultrasound increases the mixing of the two phases and enhancing the mass-transfer[25-26]. The kinetic profile of the reaction is obtained by plotting – ln (1-X) against time. In our experimental condition, without ultrasonic irradiation (silent condition) the k_{app} values are 6.48×10^{-3}, min^{-1} but in the presence of ultrasonic condition the k_{app} values are 14.64×10^{-3}, min^{-1} and 21.18×10^{-3}, min^{-1} for 28 kHz (300W) and 40 kHz (300W), respectively (Table 2). Hence, the overall k_{app} value was increased by increasing the ultrasonic frequency in the order of 0 kHz (conventional method) <28 kHz (300W) <40 kHz (300W) for our system. Similar trend was observed by Entezari *et al* [27,28].

Influence sodium hydroxide concentrations

The rate of arylation of 1,3-dihydroxybenzene strongly depends on the strength of the sodium hydroxide. Kinetic experiments were carried out by employing 5 to 20g of NaOH (keeping 2 mL water constant) under similar reaction conditions. The kinetic profile of the reaction is obtained by k_{app} against amount of concentration of NaOH. The k_{app} value or conversion tremendously increased with increasing in basicity of OH$^-$ ion (Fig. 2). It suggests that the hydroxide ions are less solvated by water molecules and there by the k_{app} value or conversion is increase[29,30]. The reaction rate also increases with the addition of droplet of water as in other SL–PTC reactions. It is Because, the amount of the available NaOH increases, resulting in the

generation of much more anions [Ph(O$^-$Na$^+$)$_2$]. The water has a subtle influence on the basicity of the OH$^-$ and the hydration of the ion-pair

Influence of water

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 under 500 rpm and ultrasonic irradiation (40 kHz/300 W). (Fig. 3) is the plot of conversion versus volume of water (mL) for different amount 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 40% of product yield was obtained in 120 minutes of reaction; but merely with 2mL of water in the system, the product yield largely increased to 90.3%. Continuing to increase the quantity of water, the reaction rate was gradually reduced. When the amount of water was added to 15 mL, the solid–liquid system became a liquid–liquid type, and the yield
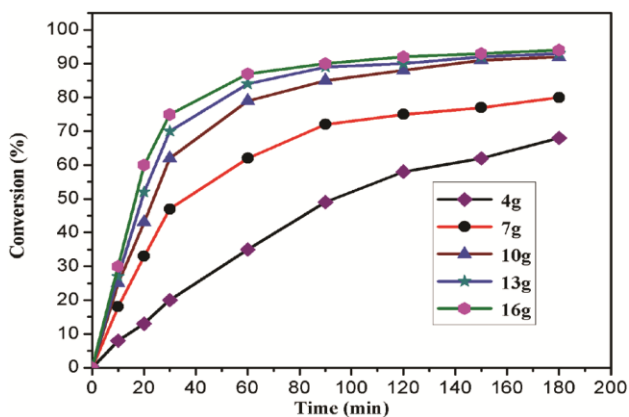

Fig. 2 — Influence of concentration of NaOH

Table 2 — Influence of Ultrasonic effect	
Ultrasonic frequency (300w)	k_{app} x 10^{-3}, min^{-1}
0 kHz	6.48
28 kHz	14.64
40 kHz	21.18

Reaction conditions: 10g of NaOH, in 2mL H$_2$O, 0.2g of biphenyl (internal standard), 45.41 mmol of 1,3-dihydroxybenzene, 20.3mmol of 1-chloro-4-nitrobenzene, 3mol% of MPTC, 30mL of chlorobenzene, 75^{0}C, 300 rpm.
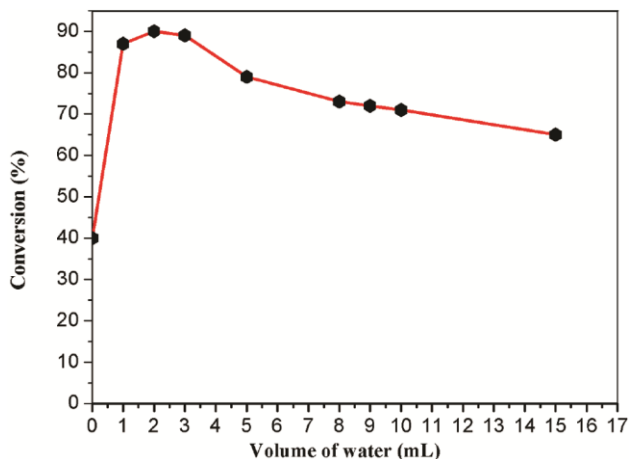

Fig. 3 — Influence of volume of water

greatly decreased to 65%, much lower than that of SLPTC. The increase of reaction rate with small amount of water was mainly due to water solubilizing a small part of solid reactant to increase the production of $Q^{2+}(Ph(O^-)_2)$ in the inter-phase, thus enhancing the intrinsic reaction rate. When more water was added, the effective concentration of $Q^{2+}(Ph(O^-)_2)$ 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 yield of 40% after 120 min of reaction. With only 2 mL of water, the formation of $Q^{2+}(Ph(O^-)_2)$ greatly increased and concentrated in the inter-phase[28] and leads to the bulk organic phase where the intrinsic reaction takes place.

Influence of the amount of prepared MPTC

The influence of the amount of MPTC (viz., 1,1,4,4-tetramethylpiperazine-1,4-diium dichloride) on the arylation of 1,3-dihydroxybenzene has been studied by varying amount of MPTC from 1 mol% to 5 mol% under ultrasound irradiation (40 kHz, 300 W) keeping the other experimental parameters constant. As shown in (Fig. 4), the rate of conversion is increased with increasing in the amount of MPTC along with ultrasound irradiation (40 kHz, 300W). The increase in the k_{app} value is attributed to the synergic effect of ultrasound, i.e. induce the surface area, change the size, and morphology of phase-transfer catalyst (MPTC). The reaction rate or conversion is increased with increasing the usage of MPTC up to 3 mol%, after that there is no remarkable increase in conversion even by increasing the amount of catalyst. It revealed that more catalyst resulted in much faster initial reaction, leads to more inorganic
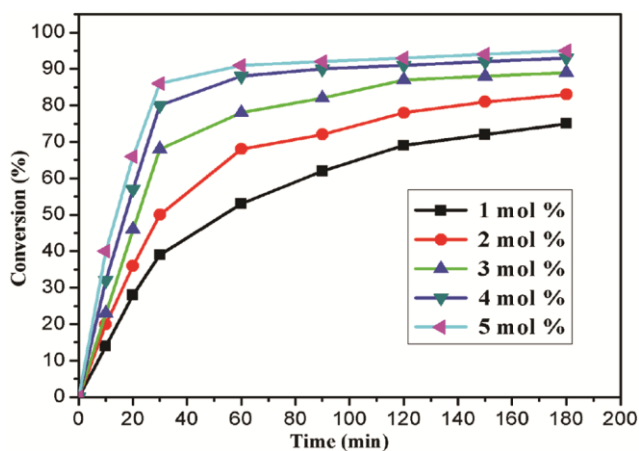

Fig. 4 — Influence of amount of Multi-site phase transfer catalyst

salt produced and deposited on the particle surface, hence reducing the contact of the catalyst and the solid reactant, and hence the reaction rate was quickly diminished and terminated in the late reaction period (>30 min) with slight deviation to pseudo-first-order kinetics. Therefore, all the further experiments were done at 3 mol% of catalyst concentration. The small amount of water (trace) can efficiently promote the solubilization of the solid reactant and thus enhance the formation of catalytic intermediate $Q^{2+}(Ph(O^-)_2)$.

Influence of concentration of 1-chloro-4-nitrobenzene

On investigating the influence of 1-chloro-4-nitrobenzene (CNB) on the kinetics of synthesis of 1,3-bis(4-nitrophenoxy)benzene under ultrasonic irradiation condition (40 kHz, 300W), the amount of 1-chloro-4-nitrobenzene (CNB) varied from 2.8g to 3.6g. The results are shown in (Table 3). The data clearly indicates that the k_{app} value increases with increase in the amount of 1-chloro-4-nitrobenzene (CNB). This observation is due to the presence of more number of active sites in the MPTC and higher concentration of substrate (CNB) had co-operatively influenced the reaction and thus enhanced the more number of contacts between catalyst and substrate (CNB), and hence it is reflected in enhanced k_{app} values. Besides ultrasound also enhances the rate of the reaction, it may be due to the reduction of the surface area between the solid and organic phase, and hence more reactants collide with each other simultaneously so that we get higher k_{app} value [31].

Influence of temperature

As for the temperature effect, the temperature varied only from 40 to 85°C keeping other operating conditions are kept constant, on the reaction of 1,3-dihydroxybenzene with 1-chloro-4-nitrobenzene. 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. The reason is that the number of

Table 3 — Influence of concentration of 1-chloro-4-nitrobenzene

1-chloro-4-nitrobenzene (g)	k_{app} x 10^{-3}, min^{-1}
2.8	16.28
3.0	18.54
3.2	21.18
3.4	23.72
3.6	26.84

Reaction conditions: 10g of NaOH, in 2mL H_2O, 0.2g of biphenyl (internal standard), 45.41 mmol of 1,3-dihydroxybenzene, 3mol% of MPTC, 30mL of chlorobenzene, 75°C, 300 rpm, ultrasound condition (40 kHz, 300W).

reactant molecules which possess higher activated energy at a higher temperature and the ultrasonic wave easily passes through the reactor.[31] 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. 5) of $-\ln k_{app}$ against $1/T$ to get activation energy o f 53.71kJ.mol^{-1}. This higher activation energy demonstrates that ultrasound assisted solid-liquid reaction with multi-site phase-transfer catalyst (MPTC) was kinetically controlled and the mass-transfer resistance between phases was unimportant. This is also an indicative of the interfacial mechanism. Hence, we proposed an interfacial mechanism for our present study.

Influence of MPTC and single-site phase-transfer catalysts

Quaternary ammonium salts are generally used as phase-transfer catalysts to promote reaction rate. Several phase-transfer catalysts were employed in addition to MPTC to evaluate their efficacy in the etherification of 1,3-dihydroxy benzene with 1-chloro-4-nitrobenzene at 75°C and 300 rpm under ultrasonic condition (40 kHz, 300W). Along with MPTC, the other six different phase-transfer catalysts were tetraoctylammonium bromide (TOAB), tetrahexylammonium bromide (THAB), tetrabutylammonium iodide (TBAI), tetrabutylammonium bromide (TBAB) and tetrabutylammonium chloride (TBAC). (Table 4) depicts the apparent rate constants for these six catalysts. Among these, MPTC shows higher reactivity as it possession two active sites of therefore the conversion is faster compared to other single site PTC's[23-17]. The greater efficiency of the MPTC is attributed to the higher lipophilic character of the
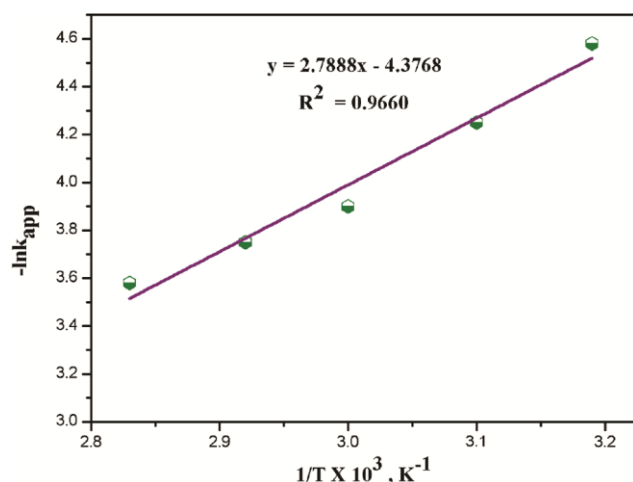
Fig. 5 — Arrhenius plot

cation (Q^{2+}) supplied by the MPTC catalyst, leading to the formation of an ion-pair $Q^{2+}(Ph(O^-)_2)$. The ion-pairs are able to enter the organic media in which the displacement reaction takes place. In general, a more oleophilic cation is more effective to transfer anions into the organic phase. Therefore, the order of catalytic reactivity are MPTC > TOAB > THAB > TBAI > TBAB > TBAC. In addition, the role of counter anion is also important. Comparing the results for TBAB, TBAC and TBAI, the order of the reactivity of these anions is $I^- > Br^- > Cl^-$. Since softer and more oleophilic anions are more effective than harder and less oleophilic anions, the order of catalytic reactivity is TBAI > TBAB> TBAC[32]. In general, the iodide of a quaternary cation is a co-catalyst, forming 1- iodo-4-nitobenzene in situation and rapidity which is more reactive than the 1-chloro-4-nitrobenzene [32].

Effect of organic solvents

The influence of various organic solvents on the rate of arylation of 1,3-dihydroxybenzene was followed under standard reaction conditions. The polarity of organic solvent affects the dissolution of solid reactant anion in organic solvent. By adding 2 mL of water, the more polar solvent induced the higher activity of phase-transfer catalyst, because a higher content of $Q^{2+}(Ph(O^-)_2)$ was acquired. From the plot of $-\ln (1-X)$ against time, the k_{app} values are obtained. It is clear from the (Table 5) chlorobenzene

Table 4 — Influence of Phase transfer catalyst

Phase transfer catalyst (3mol %)	k_{app} x 10^{-3}, min[-1]
MPTC	21.18
TOAB	16.39
THAB	14.85
TBAI	11.48
TBAB	10.12
TEAC	7.65

Reaction conditions: 10g of NaOH, in 2mL H_2O, 0.2g of biphenyl (internal standard), 15.24 mmol of indole, 13.86mmol of benzyl chloride, 30mL of chlorobenzene, 75°C, 300 rpm, ultrasound condition (40 kHz, 300W).

Table 5 — Influence of Organic solventsB

Solvents	Dielectric constant	k_{app} x 10^{-3}, min[-1]
Chlorobenzene	5.60	21.18
Ethylacetate	3.01	18.26
Toluene	2.40	12.53
Benzene	2.30	9.82
Cyclohexane	2.01	8.24

Reaction conditions: 10g of NaOH, in 2mL H_2O, 0.2g of biphenyl (internal standard), 45.41 mmol of 1,3-dihydroxybenzene, 20.3mmol of 1-chloro-4-nitrobenzene, 3mol% of MPTC, 75°C, 300 rpm, ultrasound condition (40 kHz, 300W).

possesses a higher k_{app} value among the five organic solvents used.

Conclusion

From the detailed kinetic study, the following conclusions arrived are stated here under:

- 1,3-Bis(4-nitrophenoxy)benzene was synthesized successfully from 1,3-dihydroxy benzene and 1-chloro-4-nitrobenzene(CNB) under ultrasound-MPTC condition.
- No side products were obtained during and after the reaction in all the experiments.
- The apparent reaction rates were observed to obey the pseudo-first order kinetics.
- The ultrasonic condition resulted in shorter reaction time, bis-selectivity and high yield.
- The conversion has linear relationship with increase in the temperature and the reaction was well fitted into the pseudo-first order rate equation in these temperature $(40 - 85^{0}C)$
- The suitable reaction mechanism was proposed from the experimental results.
- The apparent rate constants are increased with increase in the concentration of MPTC and NaOH, ultrasonic frequency, stirring speed and temperature.
- However it decreases with increase in the volume of water.
- Energy of activation was calculated from the Arrhenius plot.
- The combination of ultrasound and MPTC resulted in better efficacy as compared to the individual operations.

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References

1   Starks C M, Liotta C L & Halpern M C, *Top Catal*, 29 (1994) 145.
2   Dehmlow E V & Dehmlow S S, *Phase Transfer Catalysis, Monographs in Modern Chemistry.* Verlag Chemie, Weinheim, Germany (1983)
3   Sasson Y & Neumann   R, *Handbook of Phase Transfer Catalysis*, Chapman & Hall: New York (1997).
4   Wang M L & Lee Z F, *J Mol Catal A Chem*, 264 (2006) 119.
5   Hsiao H C, Kao S M & Weng H S, *Ind Eng Chem Res*, 39 (2002) 2772.
6   Mason D, Magdassi S & Sasson Y, *J Org Chem*, 56 (1991) 7229.
7   Abimannan P & Rajendran V, *Bull Chem React Eng Catal*, 11 (2016) 273.
8   Selvaraj V & Rajendran V, *Ultrason Sonochem*, 20 (2013) 1236.
9   Idoux J P, Wysocki R, Young S, Turcot J, Ohlman C & Leonard R, *Synth Commun*, 13 (1983) 39.
10 Ali H E, *Catal Commun*, 8 (2007) 855.
11 Vivekanand P A & Balakrishnan T, *Catal Commun*, 10 (2009) 1371.
12 Mason T J & Lorimer J P, *Sonochemistry: Theory, Applications and Uses of Ultrasound in Chemistry*. Ellis Horwood, Chichester (1988).
13 Loganathan S & Rajendran V, Ultrason Sonochem, 20 (2013) 308.
14 Harikumar K & Rajendran, *Ultrason Sonochem*, 21 (2014) 208.
15 Xianying S & Junfa W, *Front Chem China*, 2 (2007) 70.
16 Ge N, Zhang Y, Shi D, Gu Q, Zhu X & Ding Z, *Eur J Chem*, 2 (2011) 269.
17 Yadav G D & Sharma M M, *Ind Eng Chem Product Res Dev*, 20 (1981) 385.
18 Abimannan P & Rajendran V, *Current Catalysis*, 5 (2016) 44.
19 Doraiswamy L K & Naik S D, *Chem Eng Sci*, 52 (1997) 4533.
20 Devulapelli V G,   Weng   H S, *Cataly Commun*, 10 (2009)1638.
21 Wang, M L & Rajendran V, *J Mol Catal A chem*, 244 (2006) 237.
22 Patil R, Bhoir P, Deshpande P, Wattamwar T, Shirude M & Haskar P, *Ultrason Sonachem*, 20 (2013) 1327.
23 Murugan E & Tamizharasu G, *J Mol Catal A Chem*, 363 (2012) 81.
24 Selvaraj V & Rajendran V, *Ultrason Sonochem*, 21 (2014) 620.
25 Selvaraj V & Rajendran V, *Ultrason Sonochem*, 21 (2014) 612.
26 Kruus P, Burk R C, Entezari M H & Otson R, *Ultrason Sonochem*, 4 (1997) 229.
27 Entezari M H, Heshmati A & Yazdi A S, *Ultrason Sonochem*, 12 (2005) 137.
28 Selvaraj V, Harikumar K, Sathiyaraj M & Rajendran V, *Chem Sci J*, 6 (2015) 1.
29 Wang M L & Chen C J, *Org Process Res Dev*, 14 (2010) 737.
30 Yadav G D & Jadhav Y B, *J Mol Catal A Chem*, 192 (2003) 41.
31 Wang M L & Rajendran V, *J Mol Catal A Chem*, 273 (2007) 5.