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Synthesis of 4-(benzyloxy)biphenyl under a multi-site phase-transfer catalyst along with ultrasonication – A kinetic study

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In this present study, the synthesis of 4-(benzyloxy)biphenyl has been successfully carried out using 4-phenylphenol and benzyl chloride in the presence of ultrasonic power (40 kHz, 300W) along with synthesized multi - site phase - transfer catalyst *viz*., N^1,N^2-dibenzyl-N^1,N^1,N^2,N^2-tetramethylethane-1,2-diaminium dibromide (MPTC). The pseudo first-order kinetic equation has been applied to describe the organic reaction. The various kinetic parameters on the preparation of 4-(benzyloxy)biphenyl has been carried out under ultrasonic frequency condition and synthesized multi - site phase transfer catalyst. Sonication has resulted in better selectivity, high yield, avoids the use of the high temperature, side products and reduces the time consumption. The activation energy (Ea) has been calculated from the experimental results.

Keywords: Benzylchloride, Chloro-4-nitrobenzene, Interfacial reaction, MPTC, Ultrasound energy

To overcome the problem arises due to the mutual immiscibility of aqueous phase with the organic phase, phase transfer catalyst (PTC) is developed. PTC technique is a very well established and reported by various scientists. From the results, this work observed that the quantification of catalyst is required for effective phase-transfer action[1-2]. Apart from the various types' catalysts, PTCs are showing wide applications in drug synthesis and bring two reactants together in immiscible solvents through the complexation[3]. They also transfer the uncharged protic molecules or metal salts into the organic solvent medium for the smooth completion of the reaction. The collected reports exposed the usage of the PTC in liquid-liquid (LL-PTC) and solid-liquid (SL-PTC) organic reactions[4]. The mathematical modeling of homogeneous and heterogeneous PTC used reactions revealed the reaction information completely[5]. Additionally, the rate of PTC used chemical reaction can be improved by different methods such as electro organic synthesis, sonochemistry, microwaves and photochemistry. For the industrial applications, PTC can be used to produce organic intermediates and superior chemicals in various fields. PTC found to be one of the most effective methods in different branches of chemistry because of the simplicity, high conversion under optimum condition and the eco friendly. PTC is an economical approach to carryout reactions between two immiscible phases. It is very difficult to carryout reaction between reactants of totally immiscible, even under severe operating conditions. The low reactions rate, low conversions of the reactants can be improved by PTC methods. The reports clearly explained about the vital role of PTC as phase barriers in biphasic (heterogeneous) systems. Hence, this technique is used by the chemical industries due to the cost effective and eco friendly synthesize of various synthetic intermediates[7-9]. Efficient methods were developed through the usage of phase-transfer catalyst based on the reactant and the catalytic amounts which transfers the reactive anions into the organic phase. PTC's are potentially important as the reactions are progress with easy work-up procedure under mild conditions. Common phase transfer catalyst quaternary ammonium salts, phosphonium salts, crown ethers and cryptands[10-13]. These conventional phase transfer catalysts contain only one active site per molecule. Recently, multi-site PTC's have been synthesized and these have more than one active centre. These sites carry more aqueous molecules to react with the organic reactant and hence rate is higher than by a single site phase transfer catalyst[14-16].

Further, when the PTC reaction is carried under ultrasonic condition, it enhances the rate of the reaction. This is due to the effect of local hot spots, free radical formation and intense turbulence which raises the transfer between two immiscible phases. Use of ultrasound in a PTC reaction increases the effectiveness of the PT catalyst and selectivity of it[17]. PTC provides a methodology for organic reaction involving two or more immiscible reactants carried under ultrasound. Ultrasonication method considered as one of the eco friendly synthetic processes. This method is widely used to carry out numerous organic reactions as it accelerate mass and heat transfer between reactants[18-20] and it allow quicker and more selective reaction with better yield compared with conventional methods[21]. Ultrasound provides two cycles namely compressions and rarefaction. During rarefaction, vacuum pressure creates the cavitation bubbles and it gets destroyed in a very short period of time during compression cycle. This alternative cycle produces localized heat and high pressure[22], which enhance mass transfer and turbulent flow in liquid. Hence this method has been applied to synthetic processes especially to synthesize heterocyclic reactions[23]. Ultrasound approach creates activation energy in a micro area, thereby decreases reaction time and better yield. Hence, PTC reaction under ultrasound condition offers several advantages over traditional methods. The advantages of these approaches are high yield; enhance the reaction rate, waste minimization, mild reaction conditions[24-25].The current work focuses on the intensification of the multi-site phase transfer catalyst (MPTC) based on the reactions using ultrasound power (40kHz, 300W). The specific reaction of synthesis of 4-(benzyloxy)biphenyl from the reaction of 4-phenyl phenol and benzyl chloride using N^1,N^2– dibenzyl-N^1,N^1,N^2,N^2-tetramethylethane-1,2-diaminium dibromide as multi-site PTC in the presence of sodium hydroxide as a base.

Experimental Section

Materials

All reagents *viz.*, tetraoctylammonium bromide (TOAB), tetrabutylammonium chloride(TBAC), tetrahexylammonium bromide (THAB), tetrab utylammonium bromide (TBAB), tetrabutylamm onium iodide (TBAI), 4-phenyl phenol, benzylchloride, N^1,N^1,N^2,N^2-tetramethylethane-1,2-diamine (Aldrich), benzylbromide (Merck) biphenyl, sodium hydroxide, toluene, anisole, cyclohexane, chlorobenzene, n-hexane, ethanol, diethyl ether and other reagents for synthesis were of analaR grade (GR) chemicals and were used as such without further purification.

Instrumentation

^{1}H NMR spectra were recorded on Bruker 400 MHz using an internal deuterium lock. The compounds were dissolved in $CDCl_3$ and DMSO-d_6 as the solvents. Gas chromatography method utilized to separate and determine the compound that can be vaporized devoid of decomposition. All the synthesized compounds were analyzed using Varian gas chromatograph (GC) model 3700 with instruments with column 5% and 10 % SE-30 Chrome WHP 80/100, 3 m × 1/8” stainless steel tube and the detector is flame ionized detector. All reactions were conducted in the presence of ultrasonic frequency in digital ultrasonic cleaner tank of dimension 300 × 155 × 150 mm with liquid holding capacity of 12 L (Labman Ultrasonic cleaner, Media Instrument Manufacturing Company). The reactors have a in fuse of 28 and 40 kHz frequency with a power of 300 W. The elemental analysis of the products and the MPTC was performed on Perkin-Elmer CHNSO analyzer. The compounds compositions were used to confirm the products.

Ultrasonic bath

Ultrasonic energy cleaning bath contains water in the tank. It consisted double layers of stainless-steel material for the safety purpose. The sonochemical bath commonly used ultrasonic bath capacity of 12 L. The operating frequency of ultrasonic bath 28 kHz and 40 kHz with an output of 300W. Automatic showdown of the sonicator, i.e., 3 cm below the water level is an important. Furthermore, the pyrex glass polymers tube reactor with close-fitting outlet and the nitrogen gas. In the reaction tube an inert atmosphere was maintained by closing the outlet and inlet with rubber gaskets, and is supporting at the kernel of ultrasound cleaning bath 2 cm above from the locus of the transducer, which is perpetuated at the beneath of the bath to obtain highest ultrasound power.

Preparation of N^1, N^2-dibenzyl-N^1, N^1, N^2, N^2-tetramethylethane-1,2-diaminium dibromide

N^1, N^1, N^2, N^2– tetramethylethane-1,2-diamine (3 mL) and of benzyl bromide (5 mL) in 70mL of ethanol was kept in a 250 mL RB pyrex flask and refluxed at 60°C for 24h, the presence of N_2 atmosphere. The solvent was then eliminated completely in vacuum and quaternary onium salt, i.e

N^1, N^2– dibenzyl-N^1, N^1, N^2, N^2–tetramethylethane-1,2-diaminium dibromide(DBTMDD) (Scheme 1) was purified using n-hexane solvent and crystallized.

^{1}H NMR (500 MHz, DMSO-d_6): 7.63 - 7.55 (10H, Ar-CH), 3.79 (4H, N^+-CH_2), 4.74-4.68 (4H, Ar- CH_2), δ 3.39 (12H,CH_3).
^{13}C NMR (125 MHz, DMSO-d_6): 49.54 (CH_3), 129.10, 130.61, 133.27 (Ar-CH)55.90(CH_2), 67.16(N^+-CH_2),

Elemental analysis for $C_{20}H_{30}Br_2N_2$: Calculated (%). C 52.21, H 6.83, N 6.24, Br 34.72, Found (%). C 52.08, H 6.55, N 6.11, Br 34.25.

Synthesis of 4-(benzyloxy)biphenyl

4-Phenylphenol (3g, 17.62mmol) was added to powdered NaOH (15g) under overhead agitation for few minutes to produce 4-phenylphenol anion. To this benzylchloride (2.027g, 16.35mmol) and the synthesized N^1,N^2– dibenzyl-N^1,N^1,N^2,N^2– tetramethylethane-1,2-diaminium dibromide (MPTC) (3 mol %) in solvent like chlorobenzene (30mL) were added gradually with agitating and heated at 50°C for 2 h. The product was confirmed by thin layer chromatography. The product was separated using ethylacetate extraction and the extract was collected and solvent was evaporated under low pressure. Purified 4-(benzyloxy)biphenyl (Scheme 2) was obtain using column chromatography (packed with silica and elutent hexane and ethylacetate in 9:1 ratio). The structure was characterized by ^{1}H NMR and ^{13}C NMR spectroscopy.

^{1}H NMR (500 MHz, DMSO-d_6): δ 5.08 (2H, Ar-CH_2), 7.02-7.54 (Aromatic proton).
^{13}C NMR (125 MHz, DMSO-d_6): 70.14 (Ar-O-CH_2), 115.20, 126.79, 127.55, 128.05, 128.78, 134.08, 137.04, 140.83 (Aromatic CH), 158.42(Ar-O-CH).

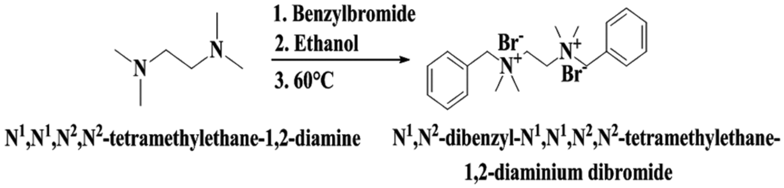
Elemental analysis for $C_{19}H_{16}O$: Calculated (%). C 87.58, H 6.04, O 6.38. Found (%).C 87.32, H 5.91, O 6.15

Sonicated Kinetics of the formation of 4-(benzyloxy)biphenyl

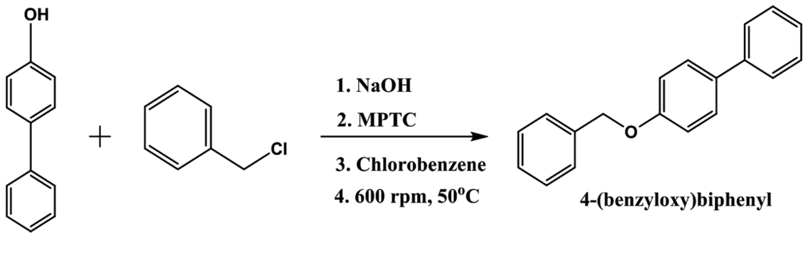
Known quantities of chlorobenzene (30mL) NaOH (15g), 0.2g biphenyl (internal standard) were placed in 500mL three neck RB flask to start the reaction. The whole setup kept in sonicator. Then, 3g (17.62mmol) of 4-phenylphenol ($C_{12}H_{10}O$), 2.027g (16.35 mmol) of benzylchloride and 0.5g of the synthesized MPTC (benzylchloride as a limiting reagent) were added in to the reactor. The reaction was agitated at 600 rpm under the influence of ultrasonic power (40 kHz, 300W). The phase separation was observed immediately after arresting the agitation method. The samples were checked by taking from the organic phase at regular intervals. A little amount of anhydrous $CaCl_2$ was placed in the sample vials to remove the aqueous traces. Varian gas chromatograph (GC) model 3700 with column of 5% and ionized detector was used to analyze the products.

Kinetic model of reaction mechanism

To prepare4-(benzyloxy)biphenyl, the overall reaction of 4-phenylphenol and benzyl chloride was



Scheme 1 — Synthesis of N^1, N^2-dibenzyl-N^1,N^1,N^2,N^2-tetramethylethane-1, 2-diaminium dibromide(MPTC)



Scheme 2 — Synthesis of 4-(benzyloxy)biphenyl catalyzed by a phase-transfer catalyst(Q^+Br) in the basic medium (NaOH) heterogeneous reaction condition is shown in Scheme 2. The reaction was carried out in ultrasound irradiation condition with MPTC. In the present study, the kinetics was followed in the existence of aminimum quantity of 4-phenylphenol and by limiting agent like benzylchloride. The purpose of conducting this reaction was to find out the change of k_{app} value of this method by using the frequency ultrasonic power (40 kHz, 300 W) under stirring speed (600 rpm)

Result and Discussion

Definition

The conversion(X) of benzylchloride(BC) is defined as follows:

$$X = 1-[BC]_o/[BC]_{o,I} \quad \dots (1)$$

where $[BC]_o$ and $[BC]_{o,I}$ represent the concentration of benzylchloride at time (t) t = 0 and t > 0,

Rate expression

The rate expression for this reaction may be expressed as:

$$-r_{BC} = K_{app}[BC]_o \quad \dots (2)$$

This reaction was carried out in a batch reactor; consequently, the diminution rate of BC with time (t) can be expressed as:

$$-d[BC]_o/[BC]_{o,I} = -r_{BC} = K_{app}[BC]_o \quad \dots (3)$$

$$-\ln \{[BC]_o/[BC]_{o,i}\} = -\ln (1-X) = K_{app} \quad \dots (4)$$

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

Effect of ultrasound and stirring on the reaction

The effect of stirring speed on the rate of O-arylation of 4-phenylphenol was examined by varying agitation speed between 100 rpm and 1000 rpm with ultrasonic power power (40kHz,300W) and newly synthesize MPTC. The significant result was observed that the rate of the reaction was enhanced linearly by increasing stirring speed from 100 to 600 rpm and above 600 rpm. The reaction rate was not changed above the stirring speed of 600 rpm. This is because of the interfacial region per unit volume of dispersal medium was increased linearly with rising the agitation speed till 600 rpm. From the results, this work observed that the raising the agitation speed modifies the atom size of the dispersed medium and no change in rate. Hence, the optimum speed was put at 600 rpm[26-29]. These results specified the effects achieved by utilising the ultrasonic power which were accountable for the improvement of the kinetics by applying strong agitation, improvement of transfer and so on. Additionally, the same reaction was conducted without applying of ultrasonic frequency and observed k_{app} value (k_{app}= 6.22 × 10^{-3}, min^{-1}, without ultrasonic condition). This value was almost 4 fold smaller than in presence of ultrasound irradiation condition (k_{app}= 23.82 × 10^{-3}, min^{-1}, 40 kHz, 300W) (Fig. 1).

Effect of the amount of multi-site phase transfer catalyst

To measure the catalyst effect, various experiments were conducted by different amounts of the MPTC by keeping other experimental parameters constant. The effect of the multi-site PTC quantity on the O-arylation of 4-phenylphenol was investigated by the addition of multi-site phase transfer catalyst range from 0.1g to 0.9g along with ultrasonic power. From the plot of –ln(1-X) versus time, the rate constant was evaluated from the linear equation which follows the pseudo first-order kinetics and have shown in Fig. 2. The reaction rate increased with increase in the quantity of multi-site PTC under ultrasonic power.

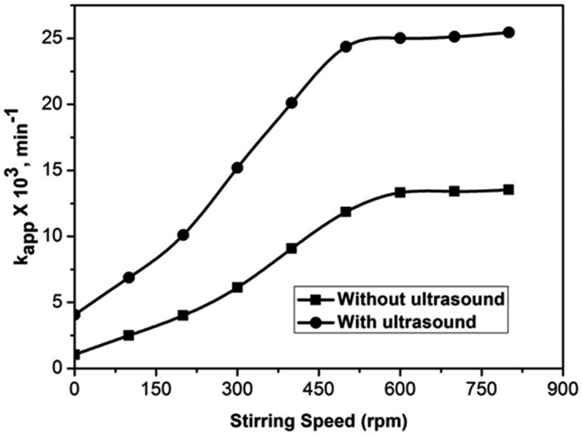


Fig. 1 — Combined effect of ultrasound and stirring on the reaction for the effect of amount of benzyl chloride(BC) with that of 4-(benzyloxy)biphenyl under ultrasonic condition. [15g of NaOH, 0.2g of internal standard (biphenyl), 0.5g of MPTC, 30 mL of chlorobenzene, 600 rpm, 50°C] .

The k_{app} values linearly depend on the amount of phase transfer catalyst.

Effect of benzylchloride concentration

Similarly, the influence of benzyl chloride on the kinetics of the 4-(benzyloxy)biphenyl along with ultrasonic irradiation condition and without ultrasonic condition examined. The amount of 1-bromobutane was added from 0.25 mL to 1.25 mL and the result has presented in Table 1. The experimental results indicated that the k_{app} value increased with increase in the quantity of benzyl chloride. This is because of benzyl chloride concentration raised the availability of reactant with better active-centre of the catalyst and thus the reaction rate was increased[29,30]. The kinetic results also specified that the increased reaction rate was observed when the reaction was carried out along ultrasonic effect[26,29]. This may be because of the reduced molecules surface area among the immiscible and therefore large a number of reactants collide with each other at the same time. This reaction showed the higher k_{app} value.

Table 1 — Effect of amount of benzyl chloride (mL)

benzyl chloride (BC), mL	$k_{app} \times 10^3$, min^{-1} (With ultrasound, 40 kHz, 300 W)	$k_{app} \times 10^3$, min^{-1} (Without ultrasound)
0.25	16.91	7.01
0.50	21.36	9.02
0.75	23.82	11.34
1.00	26.42	12.14
1.25	27.82	14.25

Effect of amount of benzyl chloride(BC) on reaction with that of 4-(benzyloxy)biphenyl under ultrasonic condition: 15g of NaOH, 0.2g of internal standard (biphenyl), 0.5g of MPTC, 30 mL of chlorobenzene, 600 rpm, 50°C; ultrasound conditions (40 kHz, 300 W).

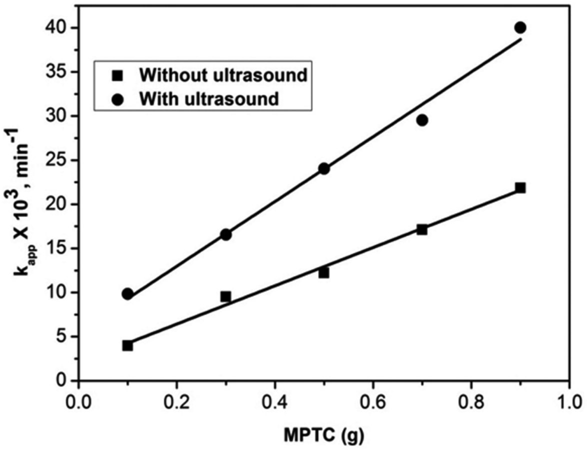


Fig. 2 — Effect of the amount of multi-site phase transfer catalyst for the reaction involving benzyl chloride (BC) with that of 4-(benzyloxy)biphenyl under ultrasonic condition. [15g of NaOH, 0.2g of internal standard (biphenyl), 30 mL of chlorobenzene, 600 rpm, 50°C; ultrasound conditions (40 kHz, 300 W)].

Effect of temperature

The effect of temperature was observed from the reaction of 4-phenylphenol and benzyl chloride by changing the temperature from 30 to 70°C. The reaction kinetics was plotted against -ln(1-X) versus time. This result was clear about the increased reactivity with a raise in the temperature under ultrasound power. The result also exposed the quantity of reactant particle which have lower energy of activation at a high heat and the ultrasonic wave simply passes through the reactor[25]. Another feature of the reaction is collision of the reactants at elevated temperature and the augmented results also observed. Therefore, at higher temperature the apparent rate constant is decreased. Arrhenius plot was plotted and represented in Fig. 3 of ($-\ln k_{app}$ against 1/T) to get an activation energy of 50.54 kJmol^{-1}.

In the reported study[31] the dehydrobromination of (2-bromoethyl) benzene reaction was catalysed by tetraoctylammonium bromide (TOAB) and the isolation mechanism was proposed due to lower Ea value< 43 kJ.mol^{-1}. In general, higher Ea (more than 43 kJ. mol^{-1}) proposed the interfacial mechanism. The interfacial mechanism of heterogeneous ethylation of phenyl acetonitrile was reported which showed the Ea of 53.64 kJ.mol^{-1} (Refs 29,32). This current study observed the Ea value for the conducted reaction in presence of MPTC was 50.54 kJ. mol^{-1}. Thus, it was proposed that interfacial mechanism occur in the organic reactions[32-35].

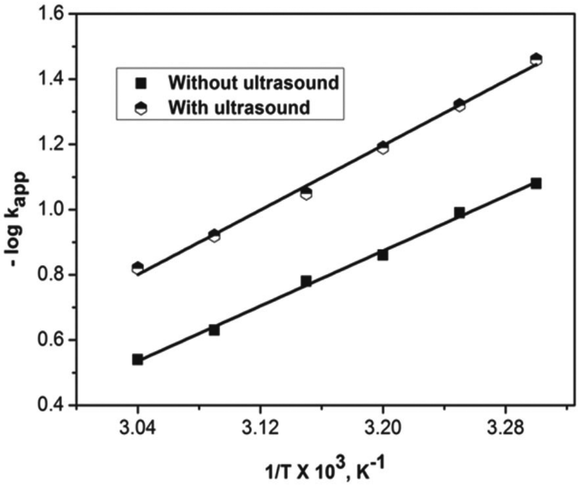


Fig. 3 — Effect of temperature (Arrhenius Plot) for the reaction involving benzyl chloride(BC) with that of 4-(benzyloxy)biphenyl under ultrasonic condition. [15g of NaOH, 0.2g of internal standard (biphenyl), 0.5g of MPTC, 30 mL of chlorobenzene, 600 rpm, ultrasound conditions (40 kHz, 300 W)].

Effect of ultrasonic power

The combination of PTC with ultrasound has been proved the good yielding and efficiency in product conversion. Ultrasound effect defined as acoustic waves creating strong electric field in the frequency range from 20 kHz to 100 MHz. The SL-PT Creaction was established to get increased by the effects of ultrasound condition. They locally generated the parameters such as elevated pressures, temperature and strong electric fields in the ultrasonic wave. This investigation used different ultrasonic frequencies like 0kHz, 28 kHz and 40 kHz for the O-arylation of 4-phenylphenol with similar 300W power. Under the same conditions, multi-site phase transfer catalyst subjected as the catalyst. Through this investigation, this work observed that the k_{app} value was $6.22 \times 10^{-3} min^{-1}$ without ultrasonic power. At same conditions, the k_{app} values were $16.85 \times 10^{-3} min^{-1}$ and $23.82 \times 10^{-3} min^{-1}$ for ultrasonic irradiation of 28 kHz, 40 kHz respectively as shown in Table 2. The usage of ultrasound energy influences the different degrees of “cavity factor”. It is the circulation of ultrasonic power through a liquid type of the reactor which makes both chemical and physical methods by acoustic cavitation.

At lower waves (less than 100 kHz), the formation of bubbles had additional time to produce more violent cavitation. Accordingly, studies were considering the mass transfer development usually for the lower frequency scope. At high frequencies, more bubbles were formed which was collapsed and created additional products[26]. Furthermore, increased ultrasound activity at high frequencies had shown in a relative study[36].

Effect of different phase-transfer catalysts

Similarly, this work also done for the effect of various PTC of quaternary onium salts as PTC improve the reaction rate. The various phase transfer catalysts such as, tetraoctylammonium bromide (TOAB), tetrahexylammonium bromide (THAB), tetrabutylammonium bromide (TBAB), tetrapropylammonium bromide (TPAB) and tetraethylammonium bromide (TEAB) were used to determine the efficiency of MPTC in the O-arylation of 4-phenyl phenol and benzyl chloride at 50°C and 600rpm. The Table 3 exposed the kinetics of 4-(benzyloxy) biphenylin occurrence of several catalysts. MPTC catalysts exhibited superior reactivity due to the existence of more active sites. Higher efficiency of catalyst was additionally credited to the strong lipophilic nature of the cation Q^{2+} which was transfered by the MPTC catalyst prominent for the creation of ion pair. These ion pairs can easily enter the organic phase where the movement of the reaction was accomplished in the order of catalytic activity of MPTC>TOAB>THAB> TBAB>TPAB> TEAB under same molar ratio of the PTC with respect to reactants. The counter anions were also participated in the cation catalytic activity.

Effect of organic solvents

In order to identify the effect of several solvents on the 4-phenylphenol and benzylchloride reaction at 50°C with 600 rpm speed using ultrasonic irradiation condition were investigated. Five different organic solvents like toluene, anisole, cyclohexane, chlorobenzene and *n*-hexane were used to study the kinetics. The higher k_{app} value was obtained for chlorobenzene among the five different solvents because its having higher dielectric constant (Table 4). Inan additional observation, it was noted that the ultrasonic frequency can be used to improve the rate in existence of more polar solvents due to the superior ultrasound power supply in reactor and created the productive collision between the reactants and catalysts. Therefore, higher k_{app} value for chlorobenzene solvent and this outcome is not satisfied for different reactants[37].

Table 2 — Effect of ultrasonic frequency (in KHt)

Ultrasonic frequency (kHz, 300W)	0	28	40
$k_{app} \times 10^3$, min^{-1}	6.22	16.85	23.82

Effect of amount of benzyl chloride(BC) with that of 4-(benzyloxy)biphenyl under ultrasonic condition: (15g of NaOH, 0.2g of internal standard (biphenyl), 0.5g of MPTC, 30 mL of chlorobenzene, 600 rpm, 50°C).

Table 3 — Effect of different phase-transfer catalysts (ing)

Phase transfer catalysts (g)	$k_{app} \times 10^3$, min^{-1} (With ultrasound, 40 kHz, 300 W)	$k_{app} \times 10^3$, min^{-1} (Without ultrasound)
MPTC	23.82	13.26
TOAB	16.54	9.35
THAB	13.89	5.14
TBAB	11.96	4.52
TPAB	9.53	3.71
TEAB	7.38	2.94

Effect of amount of benzyl chloride (BC) with that of 4-(benzyloxy)biphenyl under ultrasonic condition. [15g of NaOH, 0.2g of internal standard (biphenyl), 30 mL of chlorobenzene, 600 rpm, 50°C; ultrasound conditions (40 kHz, 300 W].

Table 4 — Effect of organic solvents (ε)

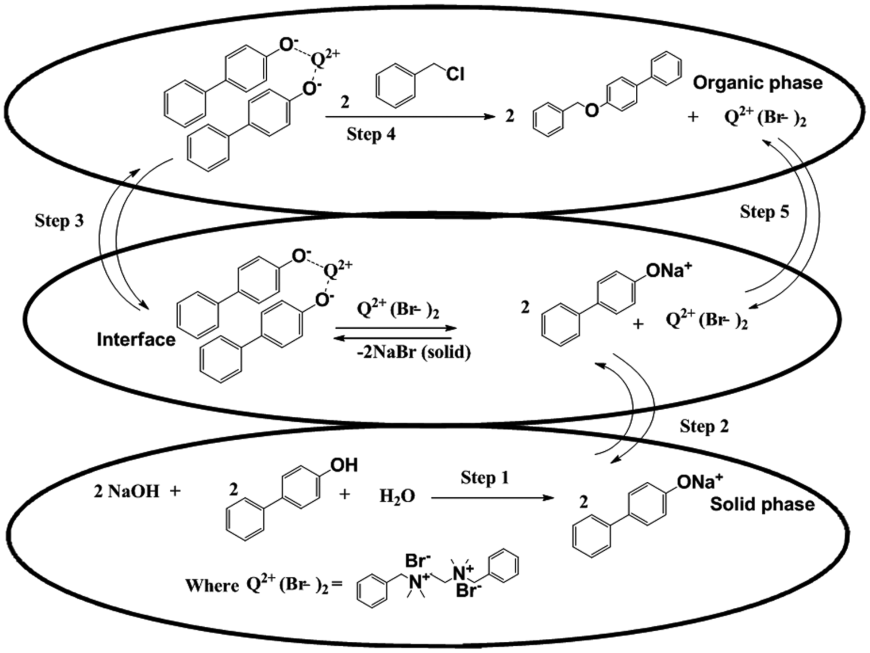
Solvents Dielectric constant (ε)	$k_{app} \times 10^3$, min^{-1} (With ultrasound, 40 kHz, 300 W)	$k_{app} \times 10^3$, min^{-1} (Without ultrasound)
Chlorobenzene 5.60	23.82	12.43
Anisole 4.30	21.61	10.21
Tolune 2.40	18.51	8.42
n-Hexane 2.28	14.24	6.86
Cyclohexane 2.01	10.02	4.69

Effect of amount of benzyl chloride(BC) with that of 4-(benzyloxy)biphenyl under ultrasonic condition: [15g of NaOH, 0.2g of internal standard (biphenyl), 600 rpm, 50°C; ultrasound conditions (40 kHz, 300 W)].

Table 5 — Effect of sodium hydroxide concentrations (ing)

Amount of NaOH(g)	$k_{app} \times 10^3$, min^{-1} (With ultrasound, 40 kHz, 300W)	$k_{app} \times 10^3$, min^{-1} (Without ultrasound)
9	15.31	7.48
12	18.45	10.12
15	23.82	13.05
18	31.63	15.87
20	40.14	19.42

Effect of amount of benzyl chloride(BC) with that of 4-(benzyloxy)biphenyl under ultrasonic condition: [0.2g of internal standard (biphenyl), 600 rpm, 50°C; ultrasound conditions (40 kHz, 300 W)].



Scheme 3 — General mechanism

Effect of sodium hydroxide concentrations

MPTC / OH $^-$catalysed reaction, the rate of the reaction was affected by alkaline compounds which have showed significant changes. The rate of 4-(benzyloxy) biphenyl powerfully depends on the concentration of NaOH (sodium hydroxide). The kinetic experiments were conducted to employ 9 to 20 g of NaOH (sodium hydroxide) for the same reaction conditions. By plotting –ln (1-X) versus time, the better kinetic results of the reaction was obtained.

The k_{app} values were extremely improved with increase in concentration of NaOH (Table 5).The outcomes revealed that the OH^- ions are less solvated by H_2O molecules at superior NaOH concentration and the activity of the OH^- ion also raise. The kinetic measurement of benzyl cyanide and *n*-bromopropane with C-alkylation reaction under PTC condition[25] rate constant significantly increased with increase in basicity of hydroxide ion. In this study, extraction of 4-phenylphenol was converted effectively in presence of ultrasound and higher concentration of NaOH.

Mechanism

From the results, it observed that the reaction rate was depending on the parameters such as stirring speed, MPTC concentration, aqueous NaOH and temperature. The observed E_a value indicated that the reaction follows inter facial mechanism (Scheme 3). Hydroxide ion (OH^-) deprotonate the 4-phenyl phenol at the interface which formed the active ion-pair $(C_{12}H_{10}O^-K^+)_2$. This ion pair exchanged its ion as $(C_{12}H_{10}O^-)_2Q^{2+}$ on the addition of catalyst $Q^{2+}(X^-)_2$. The newly formed ion pair $(C_{12}H_{10}O^-)_2\,Q^{2+}$ was highly organophili city and entered in to organic phase which reacts with the arylated agent and formed the O-arylation product 4-(benzyloxy)biphenyl.

Conclusion

The 4-(benzyloxy) biphenyl has prepared from 4-phenyphenol and benzylchloride using MPTC along with ultrasonic power (40kHz, 300W). Using the kinetic study outcomes of the organic reactions, it has been identified that the MPTC worked better under pseudo-first order kinetics. Additionally, present study has also been monitored the effect of different experimental conditions like agitation speed, substrate, base (NaOH), catalyst (MPTC), ultrasound energy, solvent and temperature. It is recognized that multi-site catalysts always improve its catalytic competence to the larger amount as compared with single – site phase transfer catalysts and therefore the MPTC's may certainly reduce the cost of the reaction method. MPTC has shown that better efficacy as compared with the commercial single-site phase transfer catalysts. The E_a has been evaluated from the Arrhenius plot. Based on the experimental results obtained the reaction mechanism has been proposed.

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References

1 Starks C M, Liotta C L & Halpern M, *Chapman Hall*, London, (1994).
2 Murugan E & Gopinath P, *J Molcatal A: Chem*, 294 (2008) 68.
3 Balakrishnan T & Murugan E, *J Appl Poly Sci*, 76 (2000) 408.
4 Balakrishnan T, Murugan E & Siva A, *J Appl Catal A: Gen*, 273 (2004) 89.
5 Sasson Y & Neumann R, *Blackie Academic*, Glasgow, (1997).
6 Dehmlow E V & Dehmlow S S, VCH, New York, (1993).
7 Selvi S, Nanthini R & Sukanya Y, *Int J Sci Tech Res*, 1 (2012) 61.
8 Rasmussen J K & Smith H K, *J Am Chem Soc*, 103 (1981) 730.
9 Wang M L & Tseng T H, *J Mol Catal A Chem*, 179 (2002) 17.
10 Sathiyaraj M &Venkatesh P, *Currorgano Catal*, 7 (2020) 89**.**
11 Balakrishnan T & Murugan E, *J Poly Sci Part A: Poly Chem*, 41 (2003) 347.
12 Siva A & Murugan A, *Synthesis*, 17 (2005) 2917.
13 Murugan A & Shanmugam P, *J Nanosci and Nanotech*, 16 (2016) 426.
14 Ali H E, *Catal Commun*, 8 (2007) 855.
15 Yang H M & ChenY C, *J Taiwan Inst Chem Eng*, 43 (2012) 897.
16 Yang H M & Chiu C, *Ultrason Sonochem*, 18 (2012) 363.
17 Sathiyaraj M, Venkatesh P & Rajendran V, *Indian J Chem Tech*, 28 (2021) 77.
18 Li J T, Chen G F, Yang W Z & Li T S, *Ultrason Sonochem*, 10 (2003) 123.
19 Gaplovsky A, Gaplovsky M, Toma S & Luche J, *J Org Chem*, 65 (200) 8444.
20 Safaei-Ghomi J, Eshteghal F & Shahbazi-Alavi H, *Ultrason Sonochem*, 33 (2016) 99.
21 Mamaghani M & Dastmard S, *Ultrason Sonochem*, 16 (2009) 445.
22 He B & Van Gerpen J H, *Bio-Fuels*, 3 (2012**)** 479.
23 Bretanha L C, Teixeira V E, Ritter M, Siqueira G M, Cunico W, Pereira C M P & Freitag R A, *Ultrason Sonochem*, 18 (2011**)** 704.
24 Li J T, Wang S X, Chen G F & Li T S, *Curr Org Synth*, 2 (2005) 415.
25 Murugesan1 V, Marimuthu E, Yoganand K S & Umapathy M J, *Int J Ind Chem*, 8 (2017) 241.
26 Bussemaker M J & Zhang D, *Ultrason Sonochem*, 21 (2014) 436.
27 Niemczewski B, *Ultrason Sonochem*, 21 (2014) 354.
28 Yang H M & Lin D W, *Cataly Commun*, 14 (2011) 101.
29 Wang M L & Rajendran V, *Ultrason Sonochem*, 14 (2007) 368.
30 Sathiyaraj M & Venkatesh P, *Bull Chem React Eng Catal*, 15 (2020) 405.
31 Halpern M, Sasson Y & Rabinovitz M, *J Org Chem*, 48 (1993) 1022.
32 Wang M L & Rajendran V, *J Mol Catal A: Chem*, 288 (2008) 23.
33 Wang M L & Lee Z F, *J Mol Catal A: Chem*, 264 (2007) 119.
34 Bhatkhande B S, Adhikari M V & Samant S D, *Ultrason Sonochem*, 9 (2002) 31.
35 Liju W, Ablajan K & Jun F, *Ultrason Sonochem*, 22 (2015) 113.
36 Entezari M H & Kruus P, *Ultrason Sonochem*, 3 (1996) 19.
37 Davidson R S, Safdar A, Spencer J D & Robinson B, *Ultrasonics*, 25 (1996) 35.