



Research Article

Synthesis of 1-butoxy-4-tert-butylbenzene under The Effect of Multi-site Phase Transfer Catalysis System – A Kinetic Study

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Abstract

Phase transfer catalysis technique proved to be a useful method for synthesizing various organic compounds under heterogeneous reactions and recognized as a viable environmentally friendly. The influence of a new multi site phase transfer catalyst (MPTC) is the synthesis of 1-butoxy-4-tertbutylbenzene from 4-tert-butylphenol with 1-bromobutane (BB) under heterogeneous solid-liquid condition using potassium hydroxide as a base at 60 °C. The higher conversion of 1-bromobutane was achieved by using the synergistic condition of multi-site phase transfer catalyst in better efficacy. The reaction rate enhanced by decreases 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, such as: MPTC, temperature, potassium hydroxide, and stirring speed. The activation energy (E_a) was also calculated through the Arrhenius plot. Copyright © 2020 BCREC Group. All rights reserved

Keywords: MPTC; phase transfer catalysis; 4-(tert-butyl)phenol; 1-bromobutane; kinetics; 1-butoxy-4-(tert-butyl)benzene

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1. Introduction

Phase transfer catalysis (PTC) has been considered as one of the better efficient tools, in the field of chemistry, because of its simplicity, high conversion, beneath very gentle reaction condition and ecofriendly nature. The PTC has been proved to be economic approach to behavior reaction among two completely immiscible reactants [1-4]. Besides this, they pose toll on environmental pollution as well PTC is an estab-

lished method in which there is an equal proportions of both aqueous with organic phases which will overcomes the difficulties associated with side product formations [5]. Recently, PTC is usually used in industrial process [6]. The economic success of chemical and related industries depends highly on the development of new process and retrofitting old process which are environmentally benign [7-8]. The advantages with phase transfer catalyst method includes easy handling of the reactions, better product yield, improved reaction rate, and specific selectivity of the reactions. Notably, these PTC based organic synthesis has wide applications in chemi-

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cal manufacturing industries, viz - pharmaceutical drugs, lubricants, pesticides, dyes, agrochemical, flavors, pollution control and monomers for polymer synthesis [9]. Moreover, PTC was employed in the chemical synthesis of oxidation, reduction, polymerizations, transition metal co-catalyzed reactions, addition and condensations reactions, *etc.* The phase transfer catalyst can be classified into two types, *i.e.* liquid-liquid biphasic PTC [10-12] and solid-liquid two phase PTC [13-14]. In this type of solid liquid phase transfer catalyst without using of water, the rate of the reaction was very elevated, almost insignificant sub-products and embrace high in yields of products.

Theory of multi-sited phase transfer catalyst (MPTC) (QX_2) was proposed by Idoux *et al.* by this reaction they have prepared phosphonium and quaternary onium ions incorporating more than one active site per molecule. The capability of the catalytic performance of these 'multi-site' PTCs towards simple S_N2 reactions and a few weak nucleophile-electrophile S_NAr reactions are have been reported [15]. The most important value for multi site PTCs is capability to transfer more number of anionic species (M^+Y^-) from aqueous phase to organic phase. In rather than the single-site quaternary onium PTC can move only one molecule of anionic species, *i.e.* M^+Y^- from aqueous phase per cycle. In particular, much insistence has been given to economy of scale and competence of onium salts mainly for the industrial scale synthesis of organic compounds. Hence, with a single active site, this commercial PTC has a limitation which is either soluble or insoluble at any given time. To overcome these limits, the growth of multi-site PTCs (MPTCs) is more advantageous because it has more than one active site with improved selectivity and specific reactivity [16]. Soluble MPTC contains two and three active sites to catalyze using the several organic reactions reported Balakrishnanan *et al.* [17-18]. Murugan *et al.* [19] also investigated kinetics of dichlorocarbene addition of citronellal using

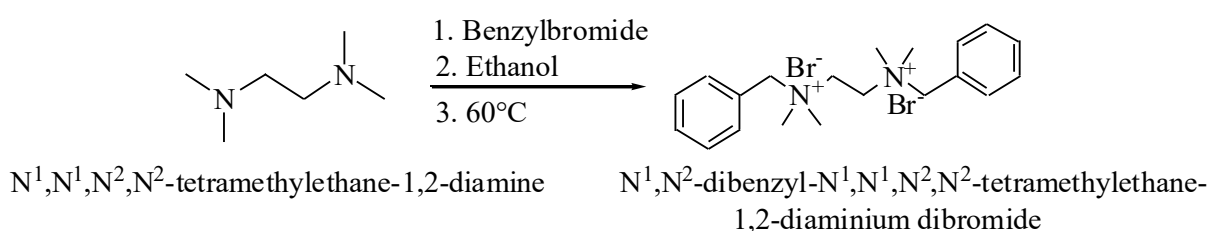
new multi-sit PTC containing two and four active sites. Wang and Lee [20] reported a kinetic study on bisphenol A and allyl bromide by using novel MPTC contain dual active site and showed that MPTC exhibit more reactivity than single site. Many author reported more than a few MPTC mediated alkylation and arylation [21-23], polymerization [24-25], epoxidation [26], asymmetric synthesis [27] reactions. N^1,N^1,N^2,N^2 -tetramethyl-ethylenediamine is an ethylenediamine derivative in which every nitrogen having two methyl groups. It is broadly employed as a catalyst in polymerization and organic reactions. It reacts with aryl halide and gives a multi-site quaternary onium phase transfer catalyst. 4-*tert*-butylphenol is a member of the class of phenols that is phenol alternate with a *tert*-butyl group at position 4. Generally, 4-*tert*-butylphenol is a phenol derivative used in the polymer industry [28].

In this present study, we have synthesized the MPTC viz. N^1,N^2 -dibenzyl- N^1,N^1,N^2,N^2 -tetramethylethane-1,2-diaminium dibromide (Scheme 1) and used as an effective catalyst for the synthesis of 1-butoxy-4-*tert*-butylbenzene from 4-*tert*-butylphenol with 1-bromobutane (BB) under heterogeneous solid-liquid condition (Scheme 2). The product obtained was confirmed by 1H NMR, ^{13}C NMR. The kinetic study of O-alkylation under controlled MPTC reaction conditions will be interesting so that the study of kinetic parameters has been followed.

2. Materials and Methods

2.1 Materials

All the reagents, including, 4-*tert*-butylphenol, 1-bromobutane, N^1,N^1,N^2,N^2 -tetramethylethane-1,2-diamine (Aldrich), benzylbromide (Merck) biphenyl, tetrabutylammonium bromide (TBAB), tetrabutylammonium chloride (TBAC), tetrabutylammonium iodide (TBAI), tetrahexylammonium bromide (THAB), tetraoctylammonium bromide (TOAB), potassium hydroxide, ethyl acetate,



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

toluene, chlorobenzene, benzene, ethanol, diethyl ether and other reagents for synthesis were of guaranteed grade (GR) chemicals and were used without further purification.

2.2 Instrumentation

^1H NMR and ^{13}C spectra were recorded using DMSO and CDCl_3 as an internal standard, respectively, on a Bruker 500 MHz. Gas Chromatography were recorded using Agilent GC-Varian 3700 model having dimension of 30 m x 0.525 mm i.d. capillary column with 100% poly(dimethyl siloxanen), injection temperature, 250 °C, FID detector (300 °C), using biphenyl as an internal standard, yield of the sample was determined.

2.3 Synthesis of A New Multi-site Phase-transfer Catalyst (MPTC)

A mixture of $\text{N}^1, \text{N}^1, \text{N}^2, \text{N}^2$ -tetramethylethane-1,2-diamine (3 g, 25.81 mmol), benzylbromide (5 g, 29.23 mmol) and 70 mL of ethanol was placed in a 250 mL three necked round bottomed Pyrex flask were refluxed at 60 °C for 24 h and in an oxygen free atmosphere. The solvent was completely removed under vacuum. The colorless solid obtained was onium salt, *i.e.* N^1, N^2 -dibenzyl- $\text{N}^1, \text{N}^1, \text{N}^2, \text{N}^2$ -tetramethylethane-1,2-diaminium dibromide, and it was washed with n-hexane and stored in a CaCl_2 packed desiccators. Yield: 96.0%; ^1H NMR (500 MHz, $\text{DMSO}-d_6$): δ 3.39 (12H, CH_3), 3.79 (4H, N^+-CH_2), 4.74-4.68 (4H, Aromatic CH_2), 7.63-7.55 (10H, Aromatic CH), ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$): 49.54 (CH_3), 55.90(CH_2), 67.16(N^+-CH_2), 129.10, 130.61, 133.27 (Aromatic CH). Elemental analysis: Calculated: C 52.20, H 6.82, N 6.22, Br 34.76, Obs (%). C 52.09, H 6.54, N 6.10, Br 34.26.

2.4 Synthesis of 1-butoxy-4-(tert-butyl)benzene

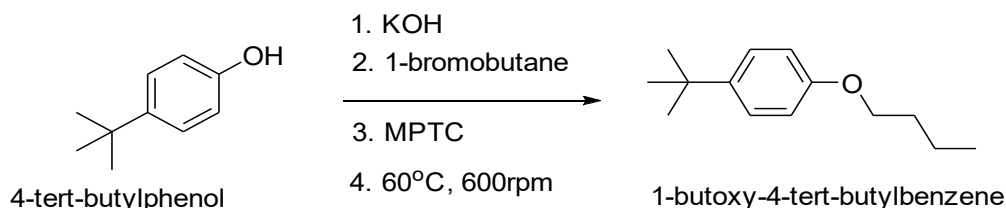
The 4-tert-butylphenol (2 g, 13.31 mmol) was added to powdered KOH (10 g in 3 mL water) under overhead stirring for few minutes to produce 4-tert-butylphenol anion. To this 1-

bromobutane (1.82 g, 13.31mmol) and the synthesized N^1, N^2 -dibenzyl- $\text{N}^1, \text{N}^1, \text{N}^2, \text{N}^2$ -tetramethylethane-1,2-diaminium dibromide (MPTC) (3 mol%) in chlorobenzene (30 mL) were added slowly with vigorous stirring and heated at 60 °C for 2 h. The product formed was evidenced by TLC. Isolation of the product was done by simple extraction ethyl acetate. Extract was collected and solvent was evaporated under reduced pressure. To obtain a pure derivative 1-butoxy-4-tert-butylbenzene the crude sample was subjected to column chromatography. The column was packed with silica and employed hexane and ethyl acetate (9:1) as an eluent. The structure was confirmed using ^1H NMR and ^{13}C NMR spectra.

^1H NMR (CDCl_3): δ 0.978 (3H- CH_3), 1.293 – 1.458 (2H-t- CH_3), δ 1.488 – 1.518 (2H- CH_2), δ 1.719 – 1.775 (2H- CH_2), δ 3.934 (2H- CH_2), δ 6.821 – 6.838 (1H-Ar-CH), δ 7.275 – 7.293 (1H-Ar-CH). ^{13}C NMR (CDCl_3): δ 14.001 (CH_3), δ 19.430, 31.164, 67.739 (CH_2), 31.679, 34.164 (t-C- CH_3), 114.072, 126.287 (Ar-CH), 143.212, 157.042 (Ar-C). Elemental analysis; Calculated: C 80.56, H 11.81, O 7.79. Obs (%). C 80.36, H 11.10, O 7.32.

2.5 Kinetics Measurements

The kinetics of reaction between well powdered KOH (10 g), biphenyl (0.2 g, internal standard), chlorobenzene (30 mL, solvent) and 4-tert-butylphenol (2 g, 13.31 mmol), 1-bromobutane (1.82 g, 13.31 mmol) in the presence newly synthesized multi-site phase transfer catalyst (3 mmol%). The reaction mixture was taken in three necked Pyrex round bottom flask (250 mL) with constant stirring at 600 rpm. Phase separation of the reaction mixture was immediate on arresting the stirring. Sample were collected from the organic layer at regular intervals of time and poured in a glass vial containing anhydrous CaCl_2 (to remove moisture) and 0.5 mL chlorobenzene. The kinetics was followed by examined the amount of 1-bromobutane (limiting agent) disappeared using gas chromatography.



Scheme 2. Synthesis of 1-butoxy-4-tert-butylbenzene.

3. Results and Discussion

3.1 Influence of Stirring Speed

With a view the influence agitation speeds on the reaction of 1-butoxy-4-tert-butyl benzene from 4-tert-butylphenol and 1-bromobutane using MPTC, the reaction was studied by varying the agitation speed range 0 to 800 rpm. There are significant increases in the reaction rate with raise in the agitation speed from 0 to 800 rpm. The rate of the reaction increases linearly as the stirring speed increases from 0-600 rpm (Table 1). Nevertheless, on further increasing the agitation speed from 600 to 800, there is no significance improvement in the reaction rate constant. Typically since the interfacial region per unit volume of scattering increased linearly with raising the agitation speed till 600 rpm is reached; there is no major increase within the interfacial region per unit volume of scattering with the comparable increase in the stirring speed. Dissolving of $C_{10}H_{13}O \cdot K^+$ in chlorobenzene increases in organic solvents with increases in agitation speed. This verify that the reaction of $C_{10}H_{13}O \cdot K^+$ and 1-bromobutane was carried out in a homogeneous solution, *i.e.* $C_{10}H_{13}O \cdot K^+$ dissolves steadily in organic solvent in the presence of multi-site phase transfer catalyst to form Q^{2+} ($C_{10}H_{13}O^-$) at interphase. Then, the formed intermediate Q^{2+} ($C_{10}H_{13}O^-$) reacted with 1-bromobutane to produce 1-butoxy-4-tert-butylbenzene in the organic phase. Thus increasing the agitation speed changes in the particle size of the dis-

Table 1. Influence of Stirring speed on the reaction condition: 10 g of KOH, in 3 mL H_2O , 0.2 g of biphenyl (internal standard), 13.31 mmol of 4-tert-butylphenol, 13.31 mmol of 1-bromobutane, 3 mol% of MPTC, 30 mL of chlorobenzene, 60 °C.

Stirring speed (rpm)	$k_{app} \times 10^{-3}, \text{min}^{-1}$
0	9.25
100	11.60
200	17.34
300	19.59
400	20.45
500	21.87
600	22.32
700	22.96
800	23.14

persed phase. Accordingly, the agitation speed was set at 600 rpm for considering the reaction occurrence from which the resistance of mass-transfer remains at a consistent esteem. Makozha and Starks [29-30] explain extraction and interfacial reaction mechanism, the two phase reaction system, the influence of stirring speed on the rate of the reaction. Wang *et al.* [31] reported the kinetic study of dichlorocyclopropanation PTC mediated dichlorocarbene addition suggested an interfacial mechanism.

3.2 Influence of Concentration of 1-bromobutane

To investigate the influence of concentration of 1-bromobutane (BB) on the kinetics of synthesis 1-butoxy-4-tert-butylbenzene under multi-site phase transfer catalyst condition, the amount of 1-bromobutane was studied that range of 1.8 to 2.6 mL keeping other experiment parameters conditions. The apparent rate constant of the reaction increases with the increases in the amount of BB was shown in Table 2. Synergetic effect of linear plot was due to further more number of active sites in MPTC and high concentration of 1-bromobutane and these increases the reaction rate. A similar result was investigated in the consideration of C-alkylation reaction of phenylacetonitrile and phenyl acetone [17] with 1-bromobutane under PTC condition.

3.3 Influence of Potassium Hydroxide Concentration

In this work, the effect of the amount of KOH on the reaction conversion of etherification was investigated. The rate of 1-butoxy-4-tert-butylbenzene powerfully depends on the potency of the potassium hydroxide. Kinetics

Table 2. Influence of concentration of 1-bromobutane on the reaction condition: 10 g of KOH, in 3 mL H_2O , 0.2 g of biphenyl (internal standard), 13.31 mmol of 4-tert-butylphenol, 3 mol% of MPTC, 30 mL of chlorobenzene, 60 °C, 600 rpm.

1-bromobutane (mL)	$k_{app} \times 10^{-3}, \text{min}^{-1}$
1.8	19.45
2.0	22.32
2.2	22.07
2.4	22.73
2.6	23.12

was carried by changing the amount of KOH from 6 to 16 g (volume of water 3 mL constant) keeping similar reaction conditions. Figure 1 gives the plot of rate constant *vs.* concentration of potassium hydroxide. The rate constant extremely increased with increase in hydroxide ion basicity, *i.e.* the rate constant was found to increase with an increase in KOH concentration. This suggests that the hydroxide ion are less solvated by water molecule and there by the activity of hydroxide ion. Balakrishnan *et al.* [16] also investigate the study of phase transfer catalyst mediated C-alkylation of indene with dibromobutane was observed rate constant extremely augmented with increase in basicity of hydroxide ion. In common, effective of the hydroxide in analyze raise due to the dependence of hydroxide basicity on hydration. Further, the reaction rate also increases with addition of droplet of water as in other SL-PTC (solid-liquid phase transfer catalyst). This is because the availability of OH⁻ increasing resulting in the formation of much more anions C₁₀H₁₃O⁻ K⁺.

3.4 Influence of Concentration MPTC

The effect of MPTC concentration (*viz.*, N¹,N²-dibenzyl-N¹,N²,N²-tetramethylethane-1,2-diaminium dibromide) on the O-alkylation of 4-tert-butylphenol was performed in the concentration range of 1 mol% to 6 mol% with all further experimental parameters kept constant. There was a comparative increase in the concentration of MPTC up to 3 mol%. The in-

fluence of amount of catalyst on reaction rate was shown in Figure 2. In common, reactivity increased with an increase in the amount of quaternary ammonium salt. It bare that more catalyst resulted in very much faster initial reaction, leads to more inorganic salt formed and deposited on the particle surface. Hence, reducing compose contact with the catalyst and the solid reactant, and hence the reaction rate was rapidly diminish and concluded in the late reaction period (>30 min) with small divergence to pseudo-first-order kinetics. The small amount of water (trace) can capably encourage the solubilization of the solid reactant and thus improve the formation of catalytic intermediate Q²⁺ (C₁₀H₁₃O⁻ K⁺).

3.5 Influence of Temperature

As for the influence of temperature on their action between 4-tert-butylphenol and 1-bromobutane was carried out in the temperature range of 20–60 °C keeping the other experimental parameters. It is clear that the reactivity is increased with an increase in the temperature, and it follows a pseudo first order rate law (Figure 3). Usually, the etherification is endothermic without any side reaction. The solubility of aqueous phase the reactant of 4-tert-butylphenol in the aqueous phase augmented by increasing the temperature. Hence, at higher temperature the apparent rate constant is increased. Arrhenius plot is given by plotting $-\ln k_{app}$ against temperature shown in Figure 4. From this $E_a = 56.71 \text{ kJ}\cdot\text{mol}^{-1}$ was cal-

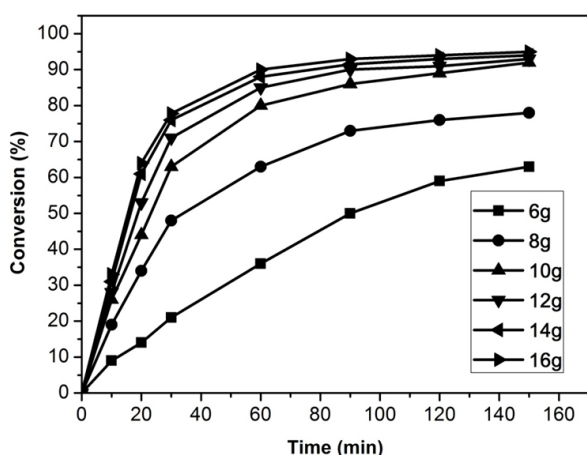


Figure 1. Influence of potassium hydroxide concentration on the apparent rate constant: 0.2 g of biphenyl (internal standard), 13.31mmol of 4-tert-butylphenol, 13.31 mmol of 1-bromobutane, 3 mol% of MPTC, 30 mL of chlorobenzene, 60 °C, 600 rpm.

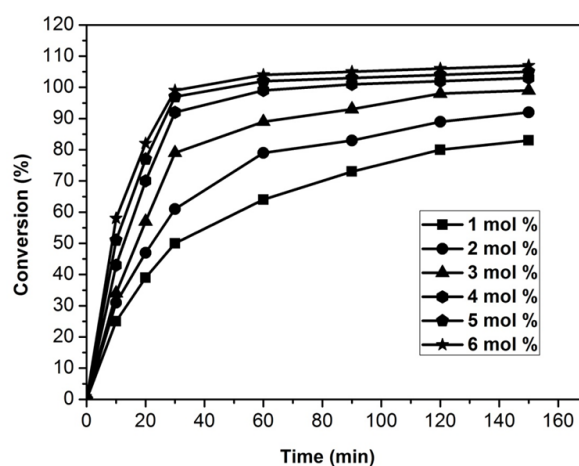


Figure 2. Influence of amount of Multi-site phase transfer catalyst on the apparent rate constant: 10 g of KOH, in 3 mL H₂O, 0.2 g of biphenyl (internal standard), 13.31 mmol of 4-tert-butylphenol, 13.31 mmol of 1-bromobutane, 30 mL of chlorobenzene, 60 °C, 600 rpm.

culated. If the reaction was under chemical reaction control condition, activation energy would be larger than 10 kcal/mol and if mass-transfer control condition, activation energy was less than 10 kcal/mol. MPTC assisted solid-liquid reaction was kinetically controlled and so the mass transfer in the interface influence of increases the activation energy. Hence, apparent activation energy value proves that the etherification reaction is under chemical reaction control with high agitation speed.

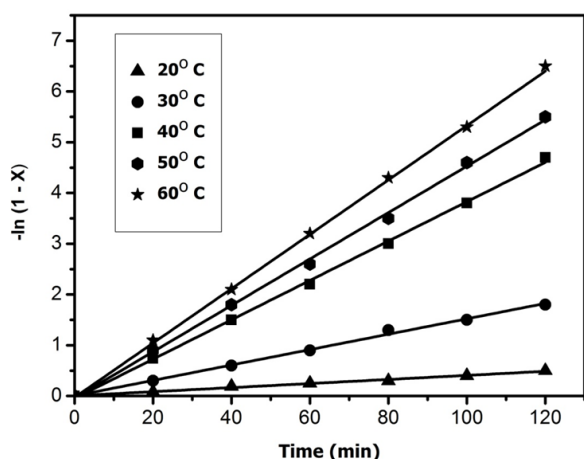


Figure 3. Influence of the temperature on the apparent rate constant: 10 g of KOH, in 3 mL H₂O, 0.2 g of biphenyl (internal standard), 13.31 mmol of 4-tert-butylphenol, 13.31 mmol of 1-bromobutane, 3 mol% of MPTC, 30 mL of chlorobenzene, 600 rpm.

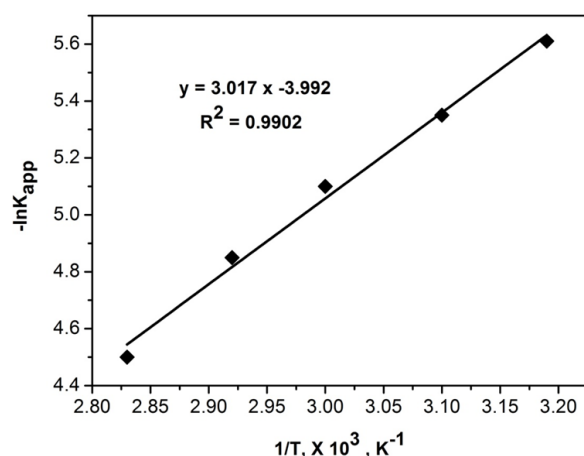


Figure 4. Arrhenius plot; 10 g of KOH in 3 mL H₂O, 0.2 g of biphenyl (internal standard), 13.31 mmol of 4-tert-butylphenol, 13.31 mmol of 1-bromobutane, 3 mol% of MPTC, 30 mL of chlorobenzene, 600 rpm.

3.6 Influence of Volume of Water

The effect of volume of water on the rate of the etherification was investigated in the range of 0 to 15 mL 10 g of KOH. The reaction was found to be pseudo first order rate law. The plot of product conversion versus volume of water is given Figure 5. The apparent rate constant slightly increased with an increase in the volume of water (0-15 mL) and then decreased with further increases in the amount of water (3-15 mL). In the absence of water, the product yield was about 40% in 120 min, so that it was enormously increased to 90.3% by just 3 mL of water in system combined addition of water to 15 mL, and the reaction rate gradually reduced. Addition of 3 mL of water increases the rate attributed to water solubility a part of solid reactant to the formation Q²⁺ (C₁₀H₁₃O·K⁺) in the interface require and thus enhance the reaction rate. Increased addition of water decreases the effective concentration of Q²⁺ (C₁₀H₁₃O·K⁺) in the interface and thereby decreasing the rate of the reaction. The reaction was sluggish in the absence of water yielding a low percentage of product formation. The formation of Q²⁺ (C₁₀H₁₃O·K⁺) is maximum and concentrated in the interface leads to bulk organic phase reaction at 3 mL optimum volume of water.

3.7 Influence of Various Phase-Transfer Catalysts

Quaternary ammonium salts are used as a phase-transfer catalysts to improve the reac-

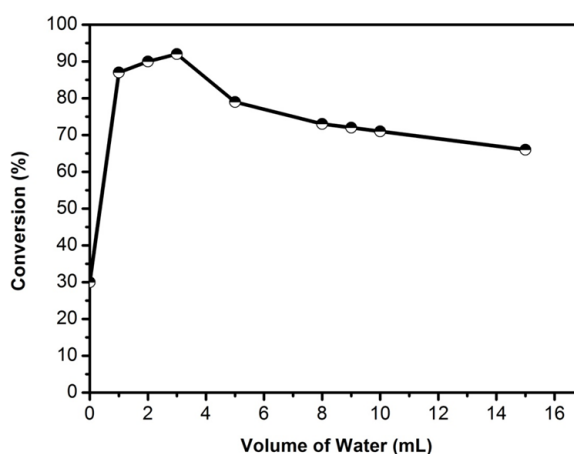


Figure 5. Influence of the volume of water on the apparent rate constant: 10 g of KOH, 0.2 g of biphenyl (internal standard), 13.31 mmol of 4-tert-butylphenol, 13.31 mmol of 1-bromobutane, 3 mol% of MPTC, 30 mL of chlorobenzene, 60 °C, 600 rpm.

tion rate. Several PTC, namely tetraoctylammonium bromide (TOAB), tetrahexylammonium bromide (THAB), tetrabutylammonium iodide (TBAI), tetrabutylammonium bromide (TBAB), and tetrabutylammonium chloride (TBAC), were employed to evaluate the efficiency of MPTC in the O-alkylation of 4-tert-butylphenol at 60 °C and 600 rpm. Table 3 shows the kinetics of 4-tert-butylphenol with 1-bromobutane in the presence of various catalysts. A various catalyst MPTC showed higher reactivity because of the presence of two active sites. The higher efficiency of MPTC further attributed to high lipophilic character of the cation Q^+ supplied by the MPTC catalyst leads to the formation of ion pair $Q^{2+}(C_{10}H_{13}O-K^+)$. The ion pairs are easily enter in to the organic phase where displacement reaction takes place order of catalytic activity of all catalysis was presented here: MPTC > TOAB > THAB > TBAI > TBAB > TBAC.

3.8 Effect of Organic Solvents

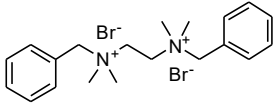
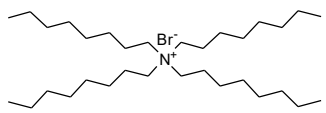
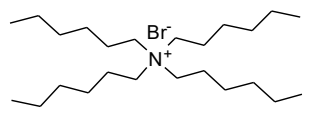
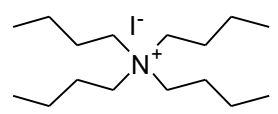
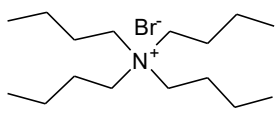
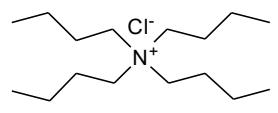
In this work, the influence of different organic solvents on the rate of O-alkylation of

4-tert-butylphenol was followed under typical reaction conditions. Dielectric constant of the medium plays an important role in bringing reaction faster. Hence, different solvents employed in this investigation are chlorobenzene, ethyl acetate, toluene, benzene, and cyclohexane dielectric constant was used to study the influence of solvent on reaction rate. The order of the relative activities of these organic solvents is as follows: chlorobenzene (C_6H_5Cl) > ethylacetate ($C_4H_8O_2$) > toluene (C_7H_8) > benzene (C_6H_6) > cyclohexane (C_6H_{10}). From Table 4, it was induced that solvent with more dielectric constant showed better rate than solvent of low dielectric constant. The increased rate constant is attributed to the increase in the dielectric constant of the organic solvent.

3.9 Reaction Mechanism

The experimental consequences from the present kinetic work specify that the dependency of the kinetic data on the whole over of agitation speed, potassium hydroxide, amount of multi-site phase transfer catalyst, temperature, and higher activation energy value are in-

Table 3. Influence of various phase transfer catalyst on the reaction condition: 10 g of KOH, in 3 mL H_2O , 0.2 g of biphenyl (internal standard), 13.31 mmol of 4-tert-butylphenol, 13.31 mmol of 1-bromobutane, 30 mL of chlorobenzene, 60 °C, 600 rpm.

Phase Transfer Catalyst (3 mol%)	Structure	$k_{app} \times 10^{-3}, \text{min}^{-1}$
MPTC		22.32
TOAB		19.25
THAB		14.58
TBAI		11.43
TBAB		9.21
TEAC		8.65

dicative of an interfacial mechanism. Mostly, the hydroxide anion deprotonates 4-tert-butylphenol at the interphase, forming an ion pair $C_{10}H_{13}O^-K^+$. In the lead addition of the catalyst (MPTC) Q^+X^- , the ion exchange has been taken place at the interfaces ($C_{10}H_{13}K^-Q^+$), and the new formed ion pair $C_{10}H_{13}K^-Q^+$

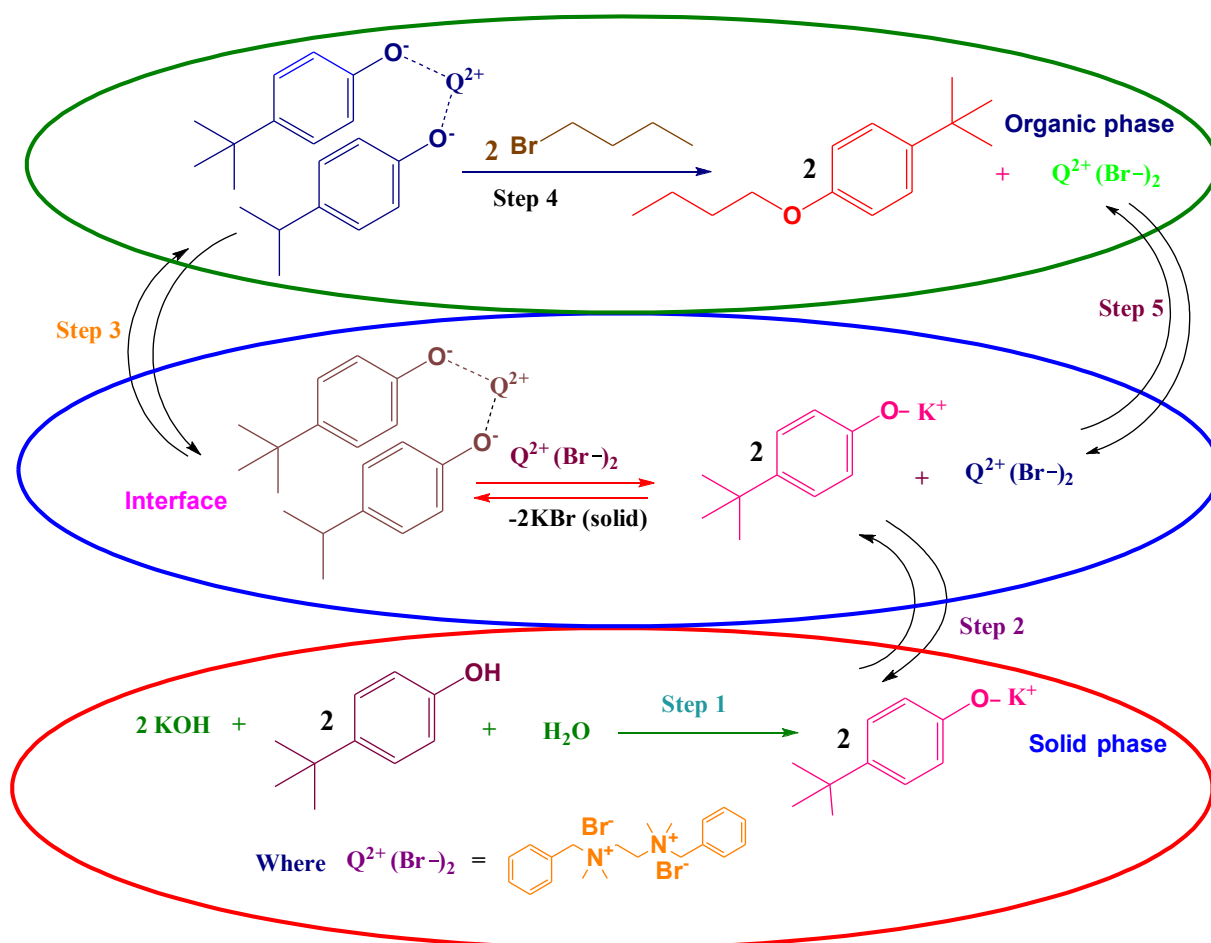
Table 4. Influence of organic solvents on the reaction condition: 10 g of KOH, in 3 mL H_2O , 0.2 g of biphenyl (internal standard), 13.31 mmol of 4-tert-butylphenol, 13.31 mmol of 1-bromobutane, 3 mol% of MPTC, 60 °C, 600 rpm.

Solvents	Dielectric constant	$k_{app} \times 10^{-3}, \text{min}^{-1}$
Chlorobenzene	5.60	22.32
Ethylacetate	3.01	18.24
Toluene	2.40	14.47
Benzene	2.30	10.82
Cyclohexane	2.01	9.43

(Scheme 3) which is an extra additional organophilicity and therefore there is an easy migration in to the organic phase. The ion pair reacts with 1-bromobutane (BB) present in the organic phase resulting in the formation of 1-butoxy-4-tert-butylbenzene as intend organic compound.

4. Conclusion

In this present work, synthesis of 1-butoxy-4-tert-butylbenzene from the reaction of from 4-tert-butylphenol and 1-bromobutane (BB) under synthesized multi-site phase transfer catalyst (MPTC) was successfully carried out using a well powdered of KOH and organic solvent biphasic medium. The appropriate reaction mechanism was verified by the experimental evidence, and the apparent rate constant was obtained from the experimental result. The apparent reaction rate was obtained to follow the pseudo first order kinetics. The apparent rate constant was found to directly dependent on every kinetic parameters, such as: multi-site phase transfer catalyst (MPTC), potassium hy-



Scheme 3. General reaction mechanism.

droxide (KOH), agitation speed, and temperature. Nevertheless, it decreases with increases in the amount of water. The reaction rate is decreased by increasing the volume of chlorobenzene. The activation energy (E_a) was also calculated through the Arrhenius plot.

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References

- [1] Rasmussen, J.K., Smith, H.K. (1981). Phase transfer free radical reactions: The Crown ether potassium peroxy disulphate initiator system. *Journal of American Chemical Society*, 103, 730-736.
- [2] Wang, M.L., Hsieh, Y.M. (2004). Kinetic study of dichlorocyclopropanation of 4-Vinyl-1-cyclohexene by a Novel Multisite Phase Transfer Catalyst. *Journal of Molecular Catalysis A: Chemistry*, 210, 59-68.
- [3] Vajjiravel, M., Umopathy, M.J. (2010). Synthesis, characterization and application of a multi-site phase transfer catalyst in radical polymerization of n-butyl methacrylate—a kinetic study. *International Journal of Polymeric Materials*, 59, 647-662.
- [4] Makosza, M., Fedorynski, M. (2012). Phase Transfer Catalysis – Basic Principles, Mechanism and Specific Features. *Current Catalysis*, 57, 79-87.
- [5] Yadav, G. D. (2004). Insight into green phase - transfer catalysis. *Topics in Catalysis*, 29, 145-161.
- [6] Jones, R.A. (2001). *Quaternary Ammonium Salts: Their Use in Phase Transfer Catalysed Reactions*. Academic Press: U.K.
- [7] Ocic, O. (2005). *Oil Refineries in the 21st Century: Energy Efficient, Cost Effective, Environmentally Benign*; John Wiley & Sons: New York.
- [8] Murugan, E., Tamizharasu, G. (2012). Synthesis and Characterization of New Soluble Multisite Phase Transfer Catalysts and Their Catalysis in Free Radical Polymerization of Methyl Methacrylate Aided by Ultrasound - A Kinetic Study. *Journal of Applied Polymer science*, 125, 263-273.
- [9] Vivekanand, P.A., Balakrishnan, T. (2009). Kinetics of dichlorocyclopropanation of vinylcyclohexane catalysed by a new multi-site phase transfer catalyst. *Catalysis Communication*, 72, 687-692.
- [10] Wang, M. L., Lee, Z.F., (2006). Reaction of 4,4-bis (chloromethyl)-1,10-biphenyl and Phenol in two-phase medium via phase-transfer catalysis. *Journal of Molecular Catalysis A: Chemistry*, 264, 19- 127.
- [11] Loganathan, S., Rajendran, V. (2013). Ultrasound assisted polymerization of N-vinyl imidazole under phase-transfer catalysis condition – A kinetic study. *Ultrasonics Sonochemistry*, 20, 308-313.
- [12] Mason, D., Magdassi, S., Sasson, Y. (1991). Role of a third liquid phase in phase-transfer Catalysis. *Journal of Organic Chemistry*, 56, 7229- 7232.
- [13] Abimannan, P., Rajendran, V. (2016). Kinetic Study for the Synthesis of 1-nitro-4-(prop-2-yn yloxy) benzene in Solid-Liquid PTC Condition. *Current Catalysis*, 5, 44-50.
- [14] Selvaraj, V., Rajendran, V. (2013). Preparation of 1,3-bis(allyloxy)benzene under a New multi- site phase-transfer catalyst combined with ultrasonication – A kinetic study. *Ultrasonics Sonochemistry*, 20, 1236-1244.
- [15] Idoux, J.P., Wysocki, R., Young, S., Turcot, J., Ohlman, C., Leonard, R. (1983). polymer-supported "multi-site" phase transfer catalysts. *Synthetic Communication*, 13, 39-144.
- [16] Vivekanand, P.A., Balakrishnan, T. (2009). Superior catalytic efficiency of a new multi-site Phase transfer catalyst in the C-alkylation of dimedone – a kinetic study. *Catalysis Communication*, 10, 1371- 1375.
- [17] Balakrishnan, T., Jeyachandran, J.P. (1995). New multi-site phase transfer catalyst for the addition of dichlorocarbene to styrene. *Journal of Chemical Society: Perkin Trans*, 2, 2081- 2085.
- [18] Balakrishnan, T., Shanmugan, K. (2007). New multi-site phase transfer catalyst for the addition of dichlorocarbene to olefins. *Indian Journal of Chemistry A*, 46, 1069-1074.
- [19] Murugan, E., Tamizharasu, G. (2012). New soluble multi-site phase transfer catalysts and their catalysis for dichlorocarbene addition to citronellal assisted by ultrasound—A kinetic study. *Journal of Molecular Catalysis A: Chemistry*, 364, 81-89.
- [20] Wang, M.L., Lee, Z.F. (2006). Synthesis of Novel Multisite Phase-Transfer Catalysts and Their Applications to the Catalyzed Reaction of Bisphenol A and Allyl Bromide. *Industrial Engineering Chemistry Research*, 45, 4918-4926.
- [21] Balakrishnan, T., Murugan, E., Siva, A. (2004). Synthesis and characterization of novel soluble multi-site phase transfer catalyst; its efficiency compared with single-site phase transfer catalyst in the alkylation of phe-

- nylacetoneitrile as a model reaction. *Applied Catalysis A: General*, 273, 89-97.
- [22] Harikumar, K., Rajendran, V. (2014). Ultrasound assisted the preparation of 1-butoxy-4-nitrobenzene under a new multi-site phase-transfer catalyst – Kinetic study. *Ultrasonics Sonochemistry*, 21, 208 – 215.
- [23] Brahmayya, M., Wang, M.L. (2016). Kinetic study for benzyloxylation of p-bromotoluene using phase transfer catalyst assisted by microwave irradiation. *Journal of Taiwan Institute of Chemical Engineering*, 000, 1–7.
- [24] Vajjiravel, M., Marimuthu, E., Yoganand, K.S., Umapathy, M.J. (2017). Multi-site phase transfer catalyzed radical polymerization of methyl methacrylate in mixed aqueous–organic medium: a kinetic study. *International Journal of Industrial Chemistry*, 8, 241–251.
- [25] Vajjiravel, M., Umapathy, M.J. (2016). Phase transfer catalyst aided radical polymerization of n-butyl acrylate in two-phase system: a kinetic study. *International Journal of Industrial Chemistry*, 7, 441–448.
- [26] Wang, M.L., Rajendran, V. (2007). Ultrasound assisted phase-transfer catalytic epoxidation of 1,7-octadiene – A kinetic study. *Ultrasonics Sonochemistry*, 14, 46–54.
- [27] Murugan, E., Siva, A. (2006). New trimeric *Cinchona* alkaloid-based quaternary Ammonium salts as efficient chiral phase transfer catalysts for enantioselective synthesis of α -amino acids. *Journal of Molecular Catalysis A: Chemistry*, 248, 1-9.
- [28] Kirsten, T.A., Olov, S., Christer, H. (2000). Tyrosinase-Mediated Formation of a Reactive Quinone from the Depigmenting Agents, 4-*tert*-Butylphenol and 4-*tert*-Butylcatechol. *Pigment Cell Research*, 13, 33-38.
- [29] Starks, M., Liotta, C.L., Halpern, M. (1994). *Phase Transfer Catalysis, Fundamentals, Applications, and Industrial Perspectives*, Chapman & Hall, New York.
- [30] Makosza, M., Fedorynski, M. (2003). Phase Transfer Catalysis. *Catalysis Reviews*, 45, 321-367
- [31] Wang, M.L., Hsieh, Y.M., Chang, R.Y. (2003). Kinetics study of dichlorocyclopropanation of 1,7-octadiene under phase transfer catalysis conditions at high alkaline concentration. *Industrial & Engineering Chemistry Research*, 42, 4702-4707.