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Preparation of Synthesis of 1-(Prop-2-Ynyloxy) Benzene Under A New Multi-Site Phase-Transfer Catalyst Combined With Ultrasonication –A Kinetic Study.

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ABSTRACT: *In the present work, kinetics of synthesis of synthesis of 1-(prop-2-ynyloxy) benzene was successfully carried out by O-propargylation of phenol with propargyl bromide using aqueous potassium hydroxide and catalyzed by a new multi - site phase - transfer catalyst viz., 1,3,5,7-tetrabenzylhexamethylenetetraminium tetrachloride, MPTC under ultrasonic (40kH_Z, 300W) assisted organic solvent condition. The pseudo first-order kinetic equation was applied to describe the overall reaction. Under ultrasound irradiation (40 kHz, 300 W) in a batch reactor, it shows that the over all reaction rates can be greatly enhanced to seven times faster with ultrasound irradiation than without using ultrasound. The present study provides a method to synthesize ethers by ultrasound assisted liquid-liquid phase-transfer catalysis.*

Keywords: *Sonocatalysis; 1-(prop-2-ynyloxy) benzene; O-propargylation; interfacial reaction; kinetics; MPTC; propargyl bromide ; Phenol.*

I. INTRODUCTION

One of the most general, efficient and environmental benign methodologies [1] that can successfully employed to solve the predicament of insolubility of aqueous phase with organic phase is the phase – transfer catalysis (PTC). As the chemical reactants reside in immiscible phases, phase- transfer catalysts have the ability to carry one of the reactants as a highly active species for penetrating the interface, into the other phase where the reaction takes place, and to give a high conversion and selectivity for the desired product under mild reaction conditions. Ever since Jarrouse and Hebd [2] found that quaternary ammonium salts as an effective catalyst for enhancing the two-phase reaction, this methodology occupies a unique niche in organic synthesis and it is a commercially matured discipline with over 600 applications [3,4] covering a wide spectrum of industries such as pharmaceuticals, agrochemicals, dyes, perfume, flavours, specialty polymers, pollution control , etc. As the application of PTC grew, much effort was placed on the development of phase - transfer catalysts with higher catalytic efficiency. To this end, researchers have developed "multi-site" phase transfer catalyst (MPTC). In this context, Idoux et al. [5] for the first time synthesized "multi – site" phosphonium PTC's as soluble and polymer- supported catalysts. MPTC catalyzed alkylation was reported by Ali [6]. The reported different multi – site PTC's for dichlorocarbene addition [7], and alkylation reactions [8].

Currently, ingenious new analytical and process experimental techniques which are environmental being techniques viz., ultrasound and microwave irradiation have become immensely popular in promoting various organic reactions [9-13]. Ultrasound irradiation is a transmission of a sound wave through a medium and is regarded as a form of energy for the excitation of reactant consequence enhances the rate of the reaction [14-16].

Application of ultrasonic waves in organic syntheses (homogeneous and heterogeneous reactions) has been boosted in recent years [17-23]. Sonication of multiphase systems accelerates the reaction by ensuring a better contact between the different phases [24,25]. Further, they also increase the reaction rate and avoid the use of high reaction temperatures [26]. These days this environmental benign technology is combined with PTC with primary objective of optimizing reaction conditions [27-29]. Palladium catalysts along with PTC proved to be excellent catalytic systems for Heck reactions involving several aryl bromides with styrene and acrylic compounds under ultrasonic conditions [30]. Yang and Peng [31] investigated the green synthesis of butyl salicylate by an efficient process of ultrasound-assisted third-liquid phase transfer catalysis in a counter current two-phase-flow reactor. Recently, Wang et al [32] the synthesis of 1-(3-phenylropyl)-pyrrolidine-2,5-dione,

which is a biologically and industrially useful imide derivative from the reaction of succinimide with 1-bromo-3-phenylpropane under ultrasound assisted solid-liquid phase-transfer catalytic almost water-free conditions.

Our interest was entered on first time evaluating the influence of ultrasound in association with phase-transfer catalyst on the synthesis of 1-(prop-2-ynyloxy) benzene by O-propargylation of phenol using propargyl bromide (PB) as a limiting agent. Since, the kinetic study of O-propargylation of phenol using propargyl bromide under controlled MPTC reaction conditions will be interesting and challenging, we followed the kinetic study of O-propargylation using 1,3,5,7-tetrabenzylhexamethylenetetraminium tetrachloride (MPTC) as catalyst under ultrasonic condition (40 kHz; 300W). Further, to best of out knowledge, there are no literature reports regarding O-proparglylation of phenol with propargyl bromide under MPTC-ultrasonic condition.

II. EXPERIMENTAL

2.1Materials

All reagents, including phenol, propargyl bromide, tetrabutylammonium bromide (TBPB), tetraethylammonium chloride (TEAC), tetraethylammonium bromide (TEPB), benzyltreithylammonium bromide (BTEPB), benzyltreithylammonium chloride (BTEAC), potassium hydroxide, toluene, chlorobenzene, biphenyl and other reagents for synthesis were guaranteed grade (GR) chemicals and were used as received without further purification.

FT-IR Spectra were recorder on a Brucker optics (model: alpha-E, German country) on KBr pellets. ^{1}H NMR and ^{13}C spectra were recorded on a Bruker DRX 400 spectrometer. Gas chromatography was carried out using a GC-Varian 3700 model.

2.2. Ultrasonic process equipment

Ultrasonic energy is transmitted to the process vessel through the liquid medium, usually water in the tank. For safety purpose, the sonochemical reactor consisted of two layers stainless steel body. The sonochemical reactor configuration used in the present work is basically an ultrasonic bath. The internal dimension of the ultrasonic cleaner tank is 48 cm x 28 cm x 20 cm with liquid holding capacity of 5 litres. Two types of frequencies of ultrasound were used in these experiments, which are 28 kHz and 40 kHz with each output as 300 W. Both ultrasounds separately produces through a flat transducer mounted at the bottom of the sonicator. In this ultrasonic instrument there is a provision for a drain as well as an outlet at the top, which gives facility of continuous operation of work. An additional heater with a facility of temperature controller has also been provided so as to facilitate some high and low temperature reactions. If the water level is lower than the outlet, i.e., 3 cm below from the top of the sonicator, the applied frequency is automatically cut off. So the water fill level is important. The reactor was a 250 mL three-necked Pyrex round-bottom flask. This reaction vessel was supported at the corner of the ultrasonic cleaning bath 2 cm above from the position of the transducer to get the maximum ultrasound energy. All the experimental parameters were done at 40 kHz with output power of 300 W.

2. 3. Synthesis of MPTC

A mixture of 7g of hexamethylenetetramine (Urotropen), 40 mL of benzyl chloride, and 60 mL of ethanol was placed in a 250 mL three necked round bottomed Pyrex flask. The reaction mixture was refluxed in the nitrogen atmosphere for 48 hours. The solvent and excess benzyl chloride were completely removed under vacuum and onium salt, i.e., 1,3,5,7-tetrabenzylhexamethylenetetrammonium tetrachloride (MPTC, Scheme 1) was washed with n- hexane (3 x 20 mL). The white solid MPTC was stored in a $CaCl_2$ desiccators. m.pt. 199°C; Yield: 90%; FT-IR: 1182 cm^{-1} (C-N^{+}); ^{1}H NMR (400 MH_Z, DMSO); δ.4.06 (s,8H-Ar-C**H$_2$**), 5.30 (s,12H, N-C**H$_2$**), 7.44-7.77 (m,20H, Ar**H**); ^{13}C NMR (100 MH_Z, DMSO): δ. 69.48 (Ar-**C**H_2), 78.77 (N-**C**H_2), 128.53, 128.76, 128.90, 129.90. (Ar-**C**) for hexamethylenetetramine (HMTA) ^{1}H NMR (400 MH_Z, DMSO): δ 4.71 (s,12H, N-C**H$_2$**); ^{13}C NMR (100 MH_Z, DMSO): δ 76.13 (N-**C**H_2).

2.4. General procedure for the synthesis of 1-(prop-2-ynyloxy) benzene under sonocatalyzed condition

To the mixture of KOH (15 g, 0.26 mol) in water (15 mL) and MPTC (0.25 g, 3.86x10^{-4} mol), phenol ((0.5 g, 5.31 mmol) was added under overhead stirring to generate the phenoxide anion. Then propargyl bromide (0.75g, 0.55ml, 6.37 mmol) in chlorobenzene (40 mL) was added slowly. The reaction mixture was heated at 45^{o}C for 6 hours with vigorous stirring. The crude product was isolated by simple extraction with diethyl ether (2 x 25 mL). The organic layer was collected and the solvent was evaporated under reduced pressure. The crude product was chromatographic (SiO_2) employing hexane: ethyl acetate (10:1) as eleunt to obtain pure monoderivative. The identity of the product was confirmed by ^{1}H NMR and ^{13}C NMR spectra of the product. ^{1}H NMR (400 MH_Z, $CDCl_3$): δ_H.7.24(m,2H),6.95(m,2H),6.83(d,J=7.8Hz,1H),6.87(d,J=2.4Hz,2H),2.51(t,J=2.4Hz,2H) ppm ^{13}C NMR (100 MH_Z, $CDCl_3$): δ. 129.67,129.50,121.61,120.75,115.30,114.93,78.64,75.47,55.77 ppm FT-IR: $\nu_{max\ /\ cm}^{-1}$, 3064, 2958, 2870, 1605, 1506, 1478, 1444, 1384, 1232, 1080, 1022, 975, 741.

2.5. Sonicated kinetics of the bi-phase reaction system

The reactor was a 150 mL three-necked Pyrex flask, serving the purposes of agitating the solution, inserting the thermometer, taking samples and feeding the feed. A known quantity of KOH (30 g, 0.53 mol) was dissolved in deionised water (30 mL) to prepare a aqueous alkaline solution. Known quantities of MPTC (0.50 g, $7.73x10^{-4}$ mol), phenol (5 g, 0.053 mol) and biphenyl (internal standard, 0.2 g) were added to reaction vessel, which was suspended in the middle of ultrasonic bath to get the maximum ultrasound energy. To form the organic phase, after stirring at 600 rpm for ten minutes at 45^{o}C, propargyl bromide (3.5 g, 0.028 mol), 30 mL of chlorobenzene (solvent) was added. To start the reaction, the aqueous and organic solution was mixed in the flask. The organic-phase sample (0.2 mL) was withdrawn from the reactor at each time interval and was put into the glass vials containing 2 mL of chlorobenzene. The contents of the reaction sample (1-(prop-2-ynyloxy) benzene and propargyl bromide) were measured by GC. The analyzing conditions are follows: GC-Varian 3700 model, Column, 30 m x 0.525 mm i.d. capillary column containing 100% poly (dimethyl siloxanen); injection temperature, 250^{0}C; FID detector (300^{0}C). Yields were determined from standard curve and using biphenyl as internal standard.

2.6. Reaction mechanism and kinetic model

For synthesizing 1-(prop-2-ynyloxy) benzene compound, the overall reaction of phenol and propargyl bromide (PB) was catalyzed by MPTC ($Q^{+}Cl^{-}$) in the aqueous alkaline (KOH) bi-phase medium and is represented in scheme 2. The reaction is carried out under MPTC assisted ultrasonic condition. Main reason for investigating the reaction in presence of ultrasonic irradiation is to find out the change of the rate of the reaction. In the current investigation the kinetics was followed in presence of excess phenol by fixing propargyl bromide as limiting agent.

2.7. Definition

The conversion (X) of Propargyl bromide (PB) is defines as follows:

$X=1-\{[PB]_{0}/[PB]_{.o,i}\}$ (1)

Where $[PB]_o$ and $[PB]_{o,i}$ represent the concentration of propargyl bromide at time (t) t=0 and t>0, respectively.

6.2 Rate expression

The rate expression for this reaction may be expressed as ;

$-r_{PB}=k_{app}[PB]_o$ (2)

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

$-d[PB]_{0}/dt = -r_{PB} = k_{app}[PB]_o$ (3)

on integrating the Eq. (3) yields:

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

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

III. RESULTS AND DISCUSSION

The reaction was conducted on a 150 mL three-necked Pyrex round-bottom flask which permits agitating the solution, inserting the water condenser to recover organic reactant and taking samples and feeding the reactants. This reaction vessel was suspended at the centre of the sonicator. A known quantity of chlorobenzene (30 mL, solvent), potassium hydroxide (0.53 mol), 0.2 g biphenyl IS, (internal standard) were introduced into the reactor. Then, 0.053 mol of phenol and 0.028 mol of propargyl bromide, 0.5g MPTC (with respect to propargyl bromide, limiting reagent) were introduced to the reactor to start the reaction. The reaction mixture was stirred at 600 rpm. The phase separation was almost immediate on arresting the stirring process. Samples were collected from the organic layer of the mixture (by stopping the stirring for 20-30 seconds each time) at regular time intervals. A pinch of anhydrous $CaCl_2$ was placed in the sample vials to PB sore any moisture present in the organic layer. Each run consisted of six samples taken over the period ranging from 5 to 30 minutes. The kinetics was followed by estimating the amount of propargyl bromide (limiting reagent) that disappeared using 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^{0}C; FID detector (300^{0}C). Yields were determined from standard curve and using biphenyl as internal standard.

3.1 Combined effect of ultrasound and stirring on the reaction

To ascertain the influence of agitation speed on the rate of O-PROP of phenol, the speed of agitation was varied in the range of 100-1000 rpm along with ultrasound irradiation (40kH$_z$, 300W) using 1,3,5,7-tetrabenzylhexamethylenetetrammonium tetrachloride as the MPTC. The result indicates that the rate of the reaction increases linearly as the agitation speed increases from 100 to 600 rpm (Fig. 1). However, on further increasing the agitation seed from 600 to 1000 rpm, there is no significant improvement in the reaction rate constant. This is because the interfacial area per unit volume of dispersion increased linearly with increasing the stirring speed till 600 rpm is reached, where there is no significant increase in the interfacial area per unit volume of dispersion with the corresponding increase in the speed. Thus, increasing the stirring speed changes the particle size of the dispersed phase. Therefore, the agitation speed was set at 600 rpm for studying the reaction phenomena from which the resistance of mass transfer stays at a constant value [30-38]. The k_{app} value is evaluated from the linear plot of –ln (1-X) versus time. The results indicate that the agitation speed had no significant influence on the apparent rate constant in the range of 600-1000 rpm. When the same reaction was carried out in the Absence of ultrasound, it was observed that the k_{app} was almost two (k_{app} = 12.8 x 10^{-3}, min^{-1}) of that obtained ultrasound conditions (k_{app} = 25.8 x 10^{-3}, min^{-1}). It is due to the effect of ultrasound irradiation (40 kHz, 300 W) can promote an intensive mixing of aqueous and organic phases, like homogeneous solution, so we get higher apparent rate constant on comparing without ultrasound.

3.2 Effect of the amount of MPTC

Experiments were conducted by varying the amount of catalyst quantity but keeping other experimental parameters constant under pseudo-first order condition. Influence of amount of MPTC on the O-propargylation of phenol has been studied by varying amount of catalyst from 0.1g to 0.9g under ultrasound irradiation (40 kHz, 300 W). Appearent rate constants were evaluated from the plot of –ln(1-X) versus time. In general, the reactivity is increased with an increase in the amount of quaternary ammonium salt. As shown in Fig. 2, the rate of the reaction increased with the increase in the amount of MPTC along with k_{app} values ultrasound irradiation (40 kHz, 300 W). The are linearly dependent on the amount of multi-site phase-transfer catalyst. The increase in the k_{app} value is attributed to the change in the size, surface area and morphology of MPTC due to the positive effect of ultrasound might be enlarged [39]. Further, the opportunity of collision between intermediates is increased by increasing MPTC amount. Therefore, the opportunity of forming a complex between them is largely increased. Hence, the apparent rate constant value increased with the increase in the amount of catalyst.

3.3 Effect of Varying Propargyl bromide Concentration

To investigate the influence of propargyl bromide (PB) on the kinetics of synthesis of 1-(prop-2-ynyloxy) benzene under sonocatalyzed reaction condition, the amount of PB was varied from 0.020 mol to 0.037 mol. In presence and Absence of ultrasound results are shown in (TPBle-1). The data clearly indicate that the k_{app} increases with increasing the concentration of propargyl bromide. When the propargyl bromide concentration increased, the probability of finding the substrate with active-site of the catalyst is enhanced and thereby the rate of the reaction increased [39]. The results also indicate an additional increase when the reaction was carried out under ultrasound condition at 40 kHz, 300 W [40]. It may be due to reduces the surface area between the aqueous and organic phases, and hence more reactants collide to each other simultaneously we get higher k_{app} value.

3.4 Effect of temperature

The effect of temperature on the reaction between phenol and propargyl bromide was studied under otherwise similar conditions. The temperature was varied from 30 to 55^{o}C. The kinetic profile of the reaction is obtained by plotting -ln (1-X) versus time (Fig 3). It is obvious that the reactivity is increased with an increase in the temperature along with ultrasonic effect [41]. The reason is that the number of reactant molecules which possess higher activation energy at a higher temperature and thus the ultrasonic wave easily passes through the reactor [42, 43]. 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. Therefore, as shown in Fig.3, the apparent rate constants are increased with an increase in the temperature along with ultrasonic condition viz., 40 kHz, 300 W. Arrhenius plots were made in Fig.4 of –ln k_{app} against 1/T to get an activation energy of 51.35 $kJ.mol^{-1}$.

From the literature survey the dehydrobromination of (2-bromoethyl) benzene catalyzed by tetraoctylammonium bromide, an extraction mechanism was proposed [44]. In general, higher activation energy suggests that contribution of intrinsic reactivity limitations is more than that of intraparticle diffusion limitations [40, 45]. The activation energy for the heterogeneous ethylation of phenylactonitrile was reported to be 83.64 kJ.mol-1and for this an interfacial mechanism was proposed [46]. In the alkylation of pyrrolidine-2-one, the Ea (51.35 $kJ.mol^{-1}$) was reported by Sasson and Bilman [47], and for this reaction they proposed an interfacial

mechanism. They concluded that the deprotonation of the substrate takes place at the interphase and consequently the organic anion is extracted and reacts in the bulk of the organic phase. The rate-determining step in the process is the anion exchange at the interphase. In our study, the observed E_a value, i.e., 51.35 kJ.mol^{-1}, indicates that the contribution of intrinsic reactivity limitations is more than that of intraparticle diffusion limitations and hence we proposed an interfacial mechanism [40, 48, 49].

3.6 Effect of Ultrasonic Power

Ultrasonic irradiation is defines as acoustic waves with frequencies in the 20 kHz -100 MHz range [20, 51]. Their energy creates cavities generating locally high temperature and pressures [52-55] or strong electric fields [53, 55-57]. Ultrasound is known to accelerate diverse types of organic reactions and it is established generous reactions, which are otherwise slow due to poor mass transfer are accelerated by sonication due to cavitation [54]. It has been reported that a combination of PTC and ultrasound is often better than either of the two techniques alone [55]. In such transfer of species across the interface and ultrasound merely facilitates this transfer, possibly by increasing the interfacial area across which this transfer occurs.

To ascertain the influence of various ultrasonic frequencies on the rate of O-propargylation of phenol with same output power of 300W, the ultrasonic frequency was varied in the range of 28 & 40 kHz under otherwise similar conditions using MPTC as the catalyst. Also we followed the reaction under silent condition. The kinetic profile of the reaction is obtained by plotting –ln(1-X) against time. In our experimental condition at 30 minutes, without ultrasonic irradiation the k_{app} values is 12.5x10^{-3}, min^{-1} but in the presence of ultrasonic condition the k_{app} values are 18.6 x 10^{-3}, min^{-1} and 25.8 x 10^{-3}, min^{-1} for 28 kHz (300 W) and 40 kHz (300 W), respectively (Table 2). The reaction rate with ultrasound irradiation (40 kHz, 300 W) was About 2 times of that without using ultrasound. In addition, different ultrasonic frequencies induce various degrees of "cavity factor". A higher frequency induces a bigger size of cavity leading to a lower threshold to promote the reaction. Hence, the overall k_{app} was increased by increasing the ultrasonic frequency in the order of 0 kHz > 28 kHz (300 W) > 40 kHz (300 W) for our system.

Similar trend was observed by Entezari and co workers [58. 59]. Ultrasound irradiation with different electric powers of 40 kHz was tested. Without the assistance of ultrasound, the k_{app} was only 12.5 x 10^{-3}, min^{-1}. With 40 kHz of ultrasound irradiation, the k_{app} value in 30 min of duration for different electric powers were 15.68 x 10^{-3}, min^{-1} for 100 W, 19.44 x 10^{-3}, min^{-1} for 200 W, and 25.8 x 10^{-3}, min^{-1} for 300 W, respectively. From the experimental result concluded that different electric powers of 40 kHz, the kapp values increased by increasing the ultrasonic electric powers of 40 kH_z.

3.7 Effect of organic solvents

In this work, the influence of various organic solvents on the rate of O-propargylation of phenol was followed under otherwise standard reaction conditions. Five organic solvents employed in this study are toluene, anisole, cyclohexane, chlorobenzene, and benzene. From the plot of –ln(1-X) against time, the kapp values are obtained. The order of reactivity for these five organic solvents is: chlorobenzene (C_6H_5Cl)> anisole ($C_7H_{16}O$)> toluene (C_7H_8) > benzene (C_6H_6)> cyclohexane (C_6H_{12}). The effect of the organic solvents on the apparent rate constants under with and without ultrasound conditions are shown in (TPBle-3). Usually, the dielectric constants are used as the main index in choosing an appropriate organic solvent. The main reason is that the effect of the organic solvent involves the solubility of the catalyst, transition state of the reaction, ion transfer, salvation, and interfacial phenomena, which are difficult to determine to a phase-transfer catalyst system. However, this statement is true for our system i.e. from the TPBle-3, chlorobenzene possesses a higher k_{app} value among the five organic solvents, due to its higher dielectric constant. In another view the ultrasonic irradiation can enhance the rate in the presence of more polar solvents due to passing higher ultrasonic waves to the reactor and makes fruitful collision between the reactants, and hence we get higher k_{app} value for chlorobenzene solvent of this system and also this statement is not always true [60].

3.8 Effect of different phase-transfer catalysts

Comprehensive comparative kinetic studies for the allylation of phenol by propargyl bromide (allylating agent) were carried out using 5 mol% various onium salts viz., 1, 3, 5, 7- tetrabenzylhexamethylenetetraminium tetrachloride. (MPTC), benzyltriethylammonium chloride (BTEAC), benzyltriethylammounium bromide (BTEPB), tetrabutylammonium bromide (TBPB), tetraethylammonium bromide (TEPB), and tetraethylammounium chloride (TEAC). The reaction was carried out under ultrasonic condition at standard reaction condition. The pseudo-first order rate constant are evaluated for all the catalyst from the plot of –ln(1-X) versus time and are presented in Table 4 with and without ultrasonic condition. According to Stark's extraction mechanism, the order of the distribution of halide ions in the organic phase is I^->Br^->Cl^-. Conversely, in the current study, order of the reactivities in choosing the TEA cation group in this work is TEAC>TEPB. Thus, higher reaction rate obtained by choosing a small size of the anionic ion in the halide groups of PTC's. Hence, this phenomenon is more consistent with the interfacial reaction mechanism rather than the extraction

reaction mechanism. For an interfacial reaction mechanism, the reaction rate is highly dependent on the concentration of the catalyst at the interface. By comparing the catalytic activity of the quaternary ammonium cations with that of the same halide ion, the order of the reactivities of these PTCs is TEA cation > BTEA cation >TBA cation. We attribute the higher reactivity obtained for TEA cation to lower total carbon number. In general, the activity of the catalyst is dependent on the structural characterises of a quaternary ammonium cation [4]. For this, the yield of the product is correlated with the accessibility of the quaternary ammonium salt, q, which is a function of carbon in each chain. Structural factors affect the formation of active catalyst cation-anion pairs between the organic phase and aqueous phase. Based on the above argument, the order of the relativities of these quaternary ammonium salts are in the order MPTC > TEAC>TEPB > BTEAC >BTEPB>TBPB. It is thus concluded that the order of the reactivity is TEA cation > BTEA cation > TBA cation, which is consistent with the result [61] obtained by Wang and Rajendran for combined with ultrasonic dichlorocarbene addition to 1, 7 – octadiene under PTC condition. The results also indicate an additional increase of k_{app} value when the reaction was carried out under ultra sound irradiation condition 40 kHz, 300W. It may be due to his change in the size, surface area and morphology of phase-transfer catalysts due to the positive effect of ultrasound [39].

3.10 Mechanism

Generally mechanism [37, 62, 63] for hydroxide ion initiated PTC reactions are classified into two types viz, (i) Starks extraction mechanism and (ii) Maksoza interfacial mechanism. In the extraction mechanism is more likely to be part of reactions when they depend agitation speed only upto certain level (300 rpm) and there after the rate will be constant factor. Also the energy of activation calculated from the Arrhenius plot will be below 42.8 $kJ.mol^{-1}$, On the other hand, if the reaction in interfacial driven reaction the rate of the reaction keep on increasing even after 300 rpm and energy activation will be above51.35 $kJ.mol^{-1}$.

The experimental result from the present kinetic study indicate the dependencies of the kinetic data on the entire stirring speed, concentration of the catalyst, aqueous potassium hydroxide and Ftemperature and higher E_a value are indicative of an interfacial mechanism. Hence we proposed an interfacial mechanism for the current study (Scheme 3). Initially, the hydroxide ion deprotonates phenol at the interface, forming an ion-pair [PhO^-K^+]. Upon addition of the catalyst, Q^+X^-, ion exchange takes place at the interface [PhO^-Q^+] and the new formed ion pair PhO^-Q^+ which is more organophilicity and hence ^{easily} migrates into the organic phase. This ion-pair reacts with the propargylating agent (PB) in the organic phase resulting in the formation of the required O-propargylate product (1-(prop-2-ynyloxy) benzene).

Scheme 1

MPTC = 1,3,5,7-Tetrabenzylhexamethylenetetraminium tetrachloride.

Scheme 2

Scheme 3

Organic

IV. FIGURES AND TABLES

Table 1
Effect of amount of Propargyl bromide

Propargyl bromide (PB), g	k_{app} x 10^3, min^{-1} (40 kHz, 300 W)
2.5	30.8
3.0	28.4
3.5	25.8
4.0	23.8
4.5	18.9

Effect of amount of Propargyl bromide (PB) on the rate of O-propargylation of phenol under ultrasonic condition: 30g of KOH, 30 mL of H_2O, 0.2g of internal standard (biphenyl), 0.0289 mol of propargyl bromide , 0.5 g of MPTC, 30 mL of chlorobenzene, 600 rpm, 45^oC; ultrasound conditions (40 kHz, 300 W).

Table 2 Effect of ultrasonic frequency

Ultrasonic frequency (kHz)	0	28	40

k_{app} x 10^3, min^{-1}	12.5	18.6	25.8

Influence of ultrasonic frequencies on the rate of O-propargylation of phenol: 0.0531mol of phenol, 30 g of KOH, 30 mL of H_2O, 0.2 g of internal standard (biphenyl), 0.0289 mol of propargyl bromide , 0.5 g of MPTC, 30 mL of chlorobenzene , 600 rpm, 45°C; ultrasound conditions (40 kHz, 300 W).

Table 3 Effect of organic solvents

	Solvents				
	Cyclohexane	benzene	Toluene	Anisole	Chlorobenzene
ε[a] (Dielectric constant)	2.02	2.28	2.31	4.30	5.60
k_{app} x 10^3, min^{-1} (40 kHz, 300 W)	10.8	13.2	18.9	23.6	25.2

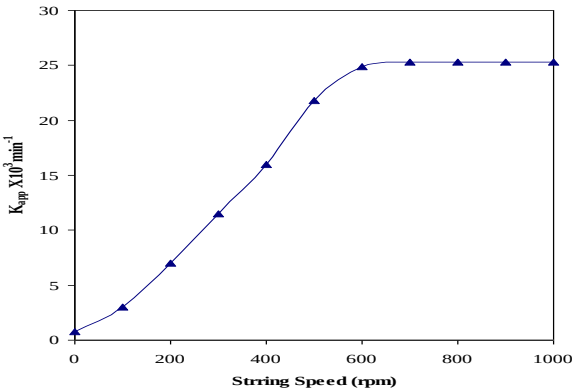
Influence of organic solvents on the rate of O-propargylation of phenol under ultrasonic condition: 0.0531mol of phenol, 30 g of KOH,30 mL of H_2O, 0.2g of internal standard (Biphenyl), 0.0289 mol of propargyl bromide , 0.5 g of MPTC, 600 rpm, 45°C; ultrasound conditions (40 kHz, 300 W).

Table 4 Effect of phase-transfer catalysts

PTC (50 mol %)	k_{app} x 10^3, min^{-1} (With ultrasound, 40 kHz, 300 W)
MPTC	25.3
TEAC	23.7
TEPB	22.4
BTEAC	20.6
BTEPB	19.5
TBPB	18.9

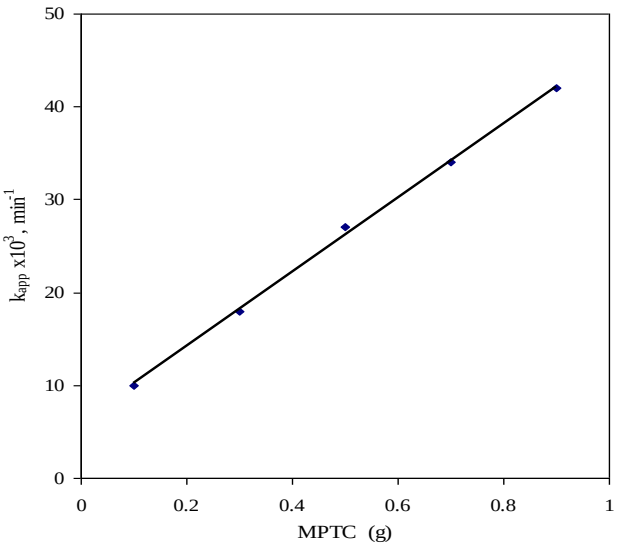
Effect of various PTC's (5 mol % based on the limiting reagent, Propargyl bromide) on the rate of O-propargylation of phenol under ultrasonic condition: 0.0531mol of phenol, 30 g of KOH, 30 mL of H_2O, 0.2 g of internal standard (biphenyl), 0.0289 mol of propargyl bromide , 30 mL of chlorobenzene , 600 rpm, 45°C; under ultrasound conditions (40 kHz, 300 W).

Figure: 1 Effect of stirring speed



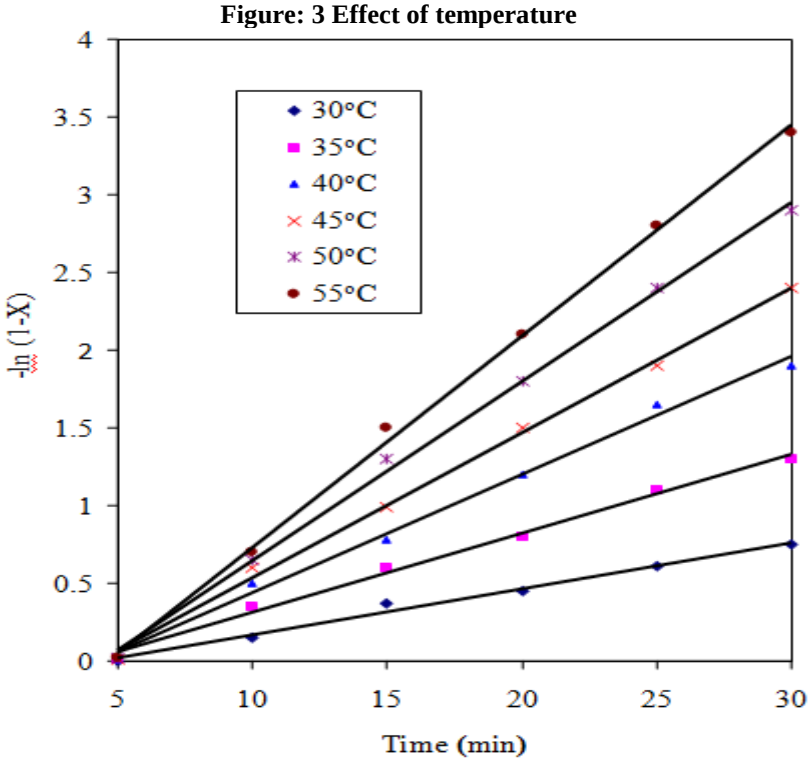
Plot of the apparent rate constant versus various stirring speeds; 0.0531mol of phenol, 30 g of KOH, 30 mL of H_2O, 0.2 g of internal standard (biphenyl), 0.0289 mol of propargyl bromide , 0.5 g of MPTC, 30 mL of chlorobenzene, 45°C; ultrasound conditions (40 kHz, 300 W).

Figure: 2 Effect of MPTC



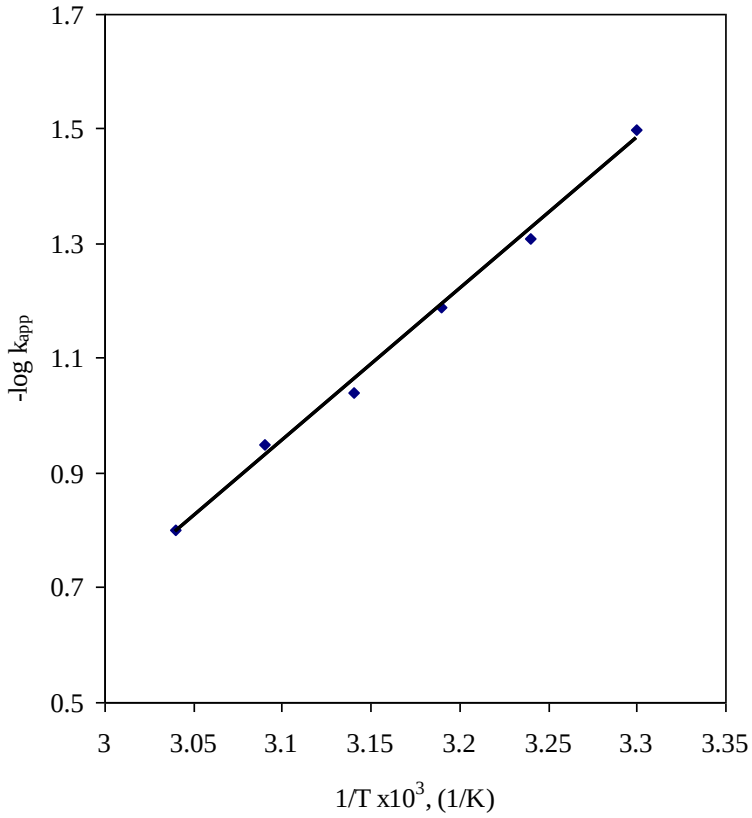
Effect of the amount of MPTC on the apparent rate constant: 0.0531mol of phenol, 30 g of KOH, 30 mL of H_2O, 0.2 g of internal standard (biphenyl), 0.0289 mol of propargyl bromide, 30 mL of chlorobenzene , 600 rpm, 45°C; ultrasound conditions (40 kHz, 300 W).

Figure: 3 Effect of temperature



Effect of temperature: 0.0531mol of phenol, 30 g of KOH, 30 mL of H_2O, 0.2 g of internal standard (biphenyl), 0.0289 mol of propargyl bromide, 30 mL of chlorobenzene , 600 rpm, 45°C; ultrasound conditions (40 kHz, 300 W).

Figure: 4 Arrhenius plot



Arrhenius plot; 0.0531mol of phenol, 30 g of KOH, 30 mL of H_2O, 0.2 g of internal standard (biphenyl), 0.0289 mol of propargyl bromide, 0.5 g of MPTC, 30 mL of chlorobenzene , 600 rpm; ultrasound conditions (40 kHz, 300 W).

V. CONCLUSION

In the present study, the reaction was controlled to study the kinetic aspects of the formation of the 1-(prop-2-ynyloxy) benzene from phenol and propargyl bromide under ultrasonic-MPTC condition. The apparent reaction rates were observed to obey the pseudo-first order kinetics, performing the reaction in ultrasonic condition resulted in shorter reaction time, selectivity high yield, etc. The reaction mechanism and the apparent rate constants were obtained from the experimental results, the apparent rate constants are found to be directly dependent on each kinetic variable, viz., [PTC], [KOH], ultrasonic frequency, stirring speed and temperature. However it decreases with increase in volume of water and phenol. Six different ammonium salts were compared under ultrasonic conditions and MPTC was found to be more efficient under given experimental conditions. Energy of activation was calculated from the Arrhenius plot. Based on the experimental evidence, an interfacial mechanism has been proposed. Combination of ultrasound and MPTC resulted in better efficacy as compared to the individual operation

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