Preparation of allyl phenyl ether 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 allyl phenyl ether was successfully carried out by O-allylation of phenol with allyl bromide using aqueous KOH and catalyzed by a new multi - site phase - transfer catalyst viz.,1,3,5,7- tetrabenzyl hexamethylene tetra minium tetrachloride, MPTC under ultrasonic (40KH$_2$, 300W) assisted organic solvent condition. O-allylation of allyl bromide has been achieved by controlling the reaction condition and has been followed by gas chromatogram. The effects of various parameters such as [stirring speed], [catalyst], [KOH], [allyl bromide], volume of water ultrasonic frequency and temperature were studied systematically to understand their influence on the rate of the reaction. The experimental observations are consistent with an interfacial-type process. Further the kinetic results demonstrate clearly, that ultrasonic assisted phase- transfer catalysis significantly increased the reaction rate when compared to conventional method.*

1. 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, flavors, 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 enhance 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]. Sonification 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.

The genesis of the current work lies in these lacunae. Our interest was entered on first time evaluating the influence of ultrasound in association with phase-transfer catalyst on the synthesis of Allyl phenyl ether by O-allylation of phenol using allyl bromide (AB) as a limiting agent. Since, the kinetic study of O-allylation of phenol using allyl bromide under controlled MPTC reaction conditions will be interesting and challenging, we followed the kinetic study of O-allylation using 1,3,5,7-tetrabenzyl hexamethylene tetra minium tetrachloride (MPTC) as catalyst under ultrasonic condition (40 kHz; 300W). Further, to best of out knowledge, there is no literature reports regarding O-allylation of phenol with allyl bromide under MPTC-ultrasonic condition.

2. Experimental
Materials

All reagents, including phenol, allyl bromide, tetrabutylammonium bromide (TBAB), tetraethylammonium chloride (TEAC), tetraethylammonium bromide (TEAB), benzyltreithylammonium bromide (BTEAB), 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.

3. Ultrasonic process equipment
Ultrasonic energy is transmitted to the process vessel through the liquid medium, usually water in the tank. For safety purpose, the sonochemical reactor consisted of two layers stainless steel body. The sonochemical reactor configuration used in the present work is basically an ultrasonic bath (model # 8425. 025.42H) equipped with flat transducer, produced from MEDICA INSTRUMENT MGF. CO. LTD., Mumbai, Indian- 400 013. The internal dimension of the ultrasonic cleaner tank is 48 cm x 28 cm x 20 cm with liquid holding capacity of 5 litres. The reactor has an operating frequency of 28 kHz and 40 kHz with a output of 300W. Both ultrasounds are separately

produced through flat transducer mounted at the bottom of the tank. 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. The process vessel is immersed in the water present in the tank.

3. 1. 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.p 199^0C; Yield: 90%; FT-IR: 1182 cm^{-1} (C-N^+); ^1H NMR (400 MH_z, DMSO); δ.4.06 (S,8H-Ar-CH_2), 5.30 (s,12H, N-CH_2), 7.44-7.77 (m,5H, ArH); ^{13}C NMR (100 MH_z, DMSO): δ. 69.48 (Ar-CH_2), 78.77 (N-CH_2), 128.53, 128.76, 128.90, 129.90. (Ar-C) for hexamethylenetetramine (HMTA) ^1H NMR (400 MH_z, DMSO): δ 4.71 (s,12H, N-CH_2); ^{13}C NMR (100 MH_z, DMSO): δ 76.13 (N-CH_2).

4. General procedure for the synthesis of allylphenylether 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 (2.5 g, 0.026 mol) was added under overhead stirring to generate the phenoxide anion. Then allyl bromide (8.75 g, 0.09 mol) in chlorobenzene (40 mL) was added slowly. The reaction mixture was heated at 45oC for 6 hours with vigorous stirring. The crude product was isolated by simple extraction with diethyl ether (2 x 25mL). The organic layer was collected and the solvent was evaporated under reduced pressure. The crude product was chromatographic (SiO2) employing hexane: ethyl acetate (10:1) as eleunt to obtain pure monoderivative. The identity of the product was confirmed by 1H NMR and 13C NMR spectra of the product. ^1H NMR (400 MH_z, $CDCl_3$): δ 4.45 (d,2H,O - CH_2), 5.34-5.39 (dd, 2H, C=CH_2), 5.64-6.05 (m, C=CH), 6.87-7.18 (m,5H,Ar-CH). ^{13}C NMR (100 MH_z, $CDCl_3$): δ. 68.77(O-CH_2), 117.59(HC=CH_2), 133.52(H_2C=CH), 114.87, 120.96, 129.96, 158.74 (Ar-CH).

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 45^0C, allyl bromide (3.5 g, 0.028 mol), 30 mL of chlorobenzene (solvent) was added. To start the reaction, the aqueous and organic solution were mixed in the flask. The organic-phase sample (0.05 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 (allyl phenyl ether and allyl bromide) were measured by GC. The analyzing conditions are as follows: GC-Varian 3700 model, The analyzing conditions were as follows; Column, 30 m x 0.525 mm i.d. capillary column containing 100% poly(dimethl siloxanen); injection temperature, 2500C; FID detector (300^{0}C). Yields were determined from standard curve and using biphenyl as internal standard.

6. Reaction mechanism and kinetic model

For synthesizing allylphenyl ether compound, the overall reaction of phenol and allyl bromide (AB) 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 allyl bromide as limiting agent.

6.1. Definition

The conversion (X) of Allyl bromide (AB) is defines as follows:

$$X=1-\{[AB]_0/[AB]_{o,i}\} \qquad 1$$

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

6.2 Rate expression

The rate expression for this reaction may be expressed as ;

$$-r_{AB}=k_{app}[AB]_o \qquad 2$$

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

$$-d[AB]_0 / dt = -r_{AB} = k_{app} [AB]_o \qquad 3$$

on integrating the Eq. (3) yields:

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

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

7. 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 allyl bromide, 0.5g MPTC (with respect to allyl 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 CaCl2 was placed in the sample vials to absorb any moisture present in the organic layer. Each run consisted of six samples taken over the period ranging from 5 to 30 minutes. The kinetics was followed by estimating the amount of allyl 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(dimethl siloxanen); injection temperature, 250^{0}C; FID detector (300^{0}C). Yields were determined from standard curve and using biphenyl as internal standard.

7.1 Effect of Stirring Speed

To ascertain the influence of agitation speed on the rate of O-allylation of phenol, the speed of agitation was varied in the range of 100-1000 rpm under otherwise similar conditions using MPTC as the catalyst. Apparent rate constants are evaluated from the linear plot of –ln(1-X) versus time. The results 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. Generally in the two-phase reaction system, the effect of stirring speed on the rate of the reaction can be explained by

(I) Starks' extraction mechanism and (ii) Makosza's interfacial reaction mechanism. Kinetic studies into effects of variation in stirring speed reveal that the interfacial mechanisms [30-36] are limited below a given stirring speed (600-800 rpm) and are intrinsic reaction rate-limited above this stirring speed. An interfacial mechanism was reported [37] for the synthesis of dichlorocyclopropane catalyzed by quaternary ammonium salt for the reaction of 1,7 –octadiene and chloroform in an alkaline solution of a NaOH/organic solvent two-phase medium. Selvaraj and Rajendaran [8] observed a linear dependence of rate constant on stirring speed upto 500 rpm for the preparation of N- benzyl imidazole are proposed an interfacial mechanism. Reactions involving extraction mechanism, proposed by Stark and Owens [38], display analogous performance but with a smaller limit of agitation speed between physical and chemical control (100-300).

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-allylation of phenol has been studied by varying amount of catalyst from 0.1g to 0.9g under ultrasound activation. 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) . The rate constants are linearly dependent on the amount of catalyst used. The increase in the k_{app} value is attributed to the change in the size, surface area and morphology of phase-transfer catalyst [39]. Further, the opportunity of collision between intermediates is increased by increasing catalyst concentration. 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.

7.3 Effect of volume of Allyl bromide

To investigate the influence of allyl bromide (AB) on the kinetics of synthesis of allyl phenyl ether under sonocatalyzed reaction condition, the amount of AB was varied from 0.020 mol to 0.037 mol. Apparent rate constants are shown in (Table-1). A similar trend was observed by Rajendran and Wang [39] for the ethoxylation of p-chloronitrobenzene using benzyltreithylammonium chloride as a phase-transfer catalyst under ultrasound irradiation conditions. Similarly Balakrishnan and Jayachandaran [40], also reported that the rate of the reaction decreases with increasing concentration of styrene for dichlorocarbene addition reaction.

7.4 Effect of temperature

The effect of temperature on the reaction between phenol and allyl bromide was studied under otherwise similar conditions. The temperature was varied from 30 to 55^{0}C. The kinetic profile of the reaction is obtained by plotting -ln (1-X) versus time (Fig 3). The rate constant increased with the increase in temperature. The energy of activation was also calculated from the Arrhenius plot; E_a = 12.04 kcal.mol^{-1} (Fig. 4). The result is consistent with results obtained previously in studies of different reaction systems [41-43]. It is evident that the rate of O-allylation increases with an increase in the temperature along with ultrasonic effect.

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 suggest 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 20 kcal.mol-1 and for this an interfacial mechanism was proposed [46]. In the alkylation of pyrrolidine-2-one, Sasson and Bilman reported [47] a higher Ea value (12.4 kcal.mol^{-1}) 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 higher E_a value, i.e., 13.20 kcal.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].

7.5 Influence of amount of water

O-allylation of phenol with allyl bromide as a limiting agent under sonocatalysis conditions was examined by varying the amount of water from 30 to 50 mL, under standard reaction conditions. Apparent rate constants were obtained from the plot of –ln(1-X) versus time. Generally, the volume of water directly affects both the concentration of KOH in the aqueous phase and also generation of anions. Therefore, the conversion (or the reaction rate) will be affected by the volume of water. Fig. 5 shows the effect of the amount of water on the rate of the reaction. On increasing the volume of water, the concentration of alkali compound in aqueous solution is decreases. This situation would dramatically reveal the hydration effect of the active catalyst [PhO$^-$Q$^+$] as the volume of water changed from 30 to 50 mL. In the kinetic study of the phase-transfer catalyzed etherification of 4,4-bis(chloromethyl)-1, 1-biphenyl with phenol in an alkaline solution of KOH/organic solvent two-phase medium, similar decrease in rate of the reaction on corresponding increase in volume of water was reported [50].

7.6 Effect of Ultrasonic Power

Ultrasonic irradiation is defines as acoustic waves with frequencies in the 20 kHz -100 MHz range [20, 51]. Their energy create 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-allylation 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) versus time. In our experiments the ultrasonic bath, model - # 8425. 025. 42H was used. At 55 minutes, without ultrasonic irradiation the rate constant is only 12.5x10^{-3}, min^{-1} but in the presence of ultrasonic the rate constants are 18.6 x 10^{-3}, min^{-1} and 25.8 x 10^{-3}, min^{-1} for 28 kHz and 40 kHz, respectively (Table 2). From these observed results, it can be inferred that ultrasonic assisted phase-transfer catalysis signifi-cantly increased the rate of the reaction. Similar trend was observed by Entezari and co workers [58. 59]. Hence, the application of ultrasounds in organic synthesis is one of the popular area in sonochemistry.

7.7 Effect of organic solvents

In this work, the influence of various organic solvents on the rate of O-allylation 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) versus time, the rate constants are obtained. The order of reactivity for these five organic solvents is: chlorobenzene (C$_6$H$_5$Cl)> anisole (C$_7$H$_{16}$O$_1$)> toluene (C$_7$H$_8$) > benzene (C$_6$H$_6$)> cyclohexane (C$_6$H$_{12}$). The effect of organic solvents on the apparent rate constant shown in Table 3. The increased rate constant is attributed to the increase in the dielectric constant (ε) of the organic solvents [60]. As the dielectric constant values of solvents increases, the activity of the

nucleophilic regent increased, hence the rate of the reaction increases.

7.8 Effect of different catalysts

Comprehensive comparative kinetic studies for the allylation of phenol by allyl bromide (allylating agent) were carried out using 5 mol% various onium salts viz., 1,3,5,7-tetrabenzylhexamethylenetetra monium tetrachloride. (MPTC), benzyltriethylammonium chloride (BTEAC), benzyltriethylammounium bromide (BTEAB), tetrabutylammonium bromide (TBAB), tetraethylammonium bromide (TEAB), 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 (entries 1-6). According to Stark's extraction mechanism, the order of the distribution of halide ions in the organic phase is l->Br->Cl-. Conversely, in the current study, order of the reactivities in choosing the TEA cation group in this work is TEAC>TEAB. 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>TEAB > BTEAC >BTEAB>TBAB. 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.

7.9 Effect of varying potassium hydroxide concentrations

In the PTC / OH- catalyzed reaction, the reaction rate is known to be greatly affected by a concentration of the alkaline compound. The rate of O-allylation of phenol strongly depends on the strength of the potassium hydroxide. Kinetic experiment were carried out, employing 20 to 40 g under similar reaction conditions. The Kinetic profile of the reaction is obtained by $-\ln(1-X)$ versus time. The rate constant tremendously increased with increase in basicity of hydroxide ion i.e., the rate constant were found to increase with an increase in potassium hydroxide concentration Table 5. It suggest that the hydroxide ions which are less solvated by water molecules and there by the activity of the hydroxide ion increases. Landine et al. [62] observed that, on increasing alkalinity concentration of, the quantity of hydroxide extracted decreases. The overall activity of the hydroxide actually increases due to the dependents of hydroxide basicity on hydration. In the kinetic study of C – alkylation of benzyl cyanide with n- bromopropane under PTC condition [63] the observed rate constant tremendously increased with increase in basicity of hydroxide ion. In our case the extraction of phenol is more effective when the base concentration is higher.

8. Mechanism

Generally mechanism [37, 63, 64] 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 10 kcal.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 above 10 kcal.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, temperature and higher E_a value are indicative of an interfacial mechanism. Hence we propose 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 and the new formed ion pair PhO⁻Q⁺ easily migrates into the organic phase. This ion pair reacts with the allylating agent in the organic phase resulting in the formation of the required O-allylated product (allyl phenyl ether).

9. Conclusion

In the present study, the reaction was controlled to study the kinetic aspects of the formation of the allyl phenyl ether from phenol and allyl bromide under ultrasonic-MPTC controlled condition. The apparent reaction rates were observed to obey the pseudo-first order kinetics. Performing the reaction in sonicatalysis condition resulted in shorter reaction time, 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., [catalyst], [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 operations.
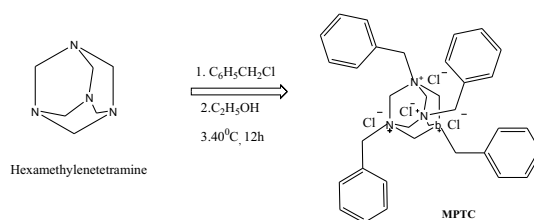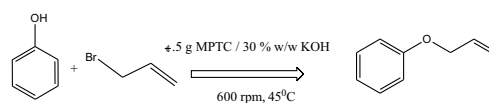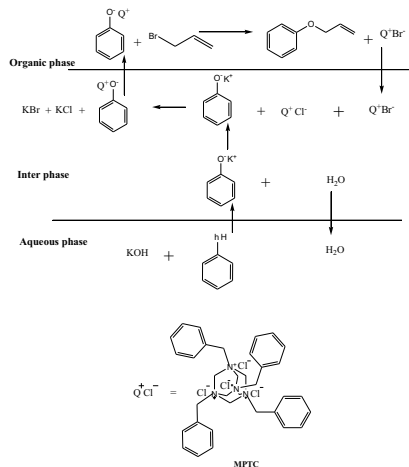
Scheme 1

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

Scheme 2

Phenol   Ally bromide   Ally phenyl ether

Scheme 3

Figure: 2

Figure: 2

Caption of figures

Fig. 1.
Plot of the apparent rate constant versus various stirring speeds; 0.0531 mol of phenol, 30 g of KOH, 30 mL of H_2O, 0.2 g of internal standard (Biphenyl), 0.0289 mol of allyl bromide, 0.5 g of MPTC, 30 mL of chlorobenzene, 45oC; ultrasound conditions (40 kHz, 300 W).

Fig. 2.
Effect of the amount of MPTC on the apparent rate constant: 0.0531 mol of phenol, 30 g of KOH, 30 mL of H_2O, 0.2 g of internal standard (Biphenyl), 0.0289 mol of allyl bromide, 30 mL of chloroben-zene, 600 rpm, 45^0C; ultrasound conditions (40 kHz, 300 W).

Fig. 3.
Effect of temperature: 0.0531 mol of phenol, 30 g of KOH, 30 mL of H_2O, 0.2 g of internal standard (Biphenyl), 0.0289 mol of allyl bromide, 30 mL of chlorobenzene, 600 rpm, 45^0C; ultrasound conditions (40 kHz, 300 W).

Figure: 3

Figure: 4

Fig. 4.
 Arrhenius plot; 0.0531 mol of phenol, 30 g of KOH, 30 mL of H_2O, 0.2 g of internal standard (Biphenyl), 0.0289 mol of allylbromide, 0.5 g of MPTC, 30 mL of chlorobenzene, 600 rpm; ultrasound conditions (40 kHz, 300 W).

Fig. 5.
Plot of the apparent rate constants versus different volumes of water; 0.0531 mol of phenol, 30 g of KOH, 0.2 g of internal standard (Biphenyl), 0.0289 mol of allyl bromide, 0.5 g of MPTC, 30 mL of chlorobenzene, 600 rpm, 45^0C; ultrasound conditions (40 kHz, 300 W).
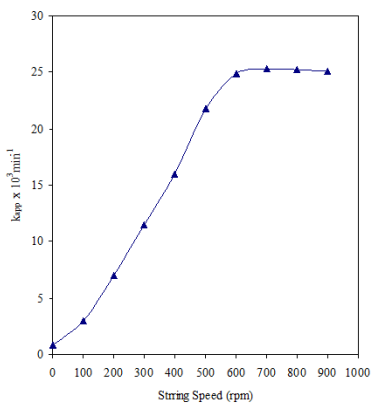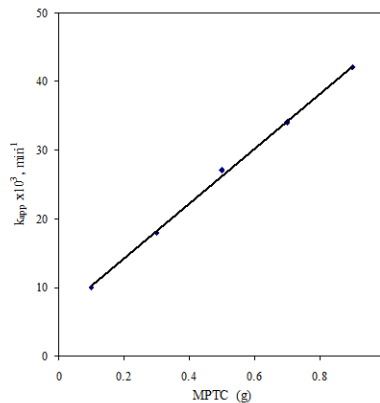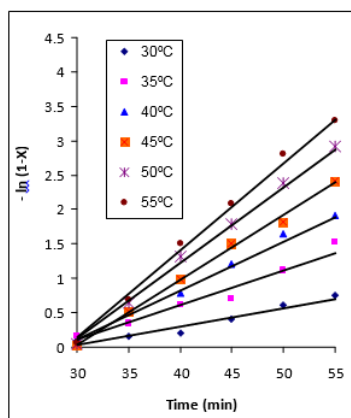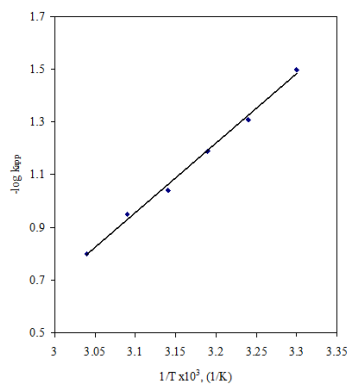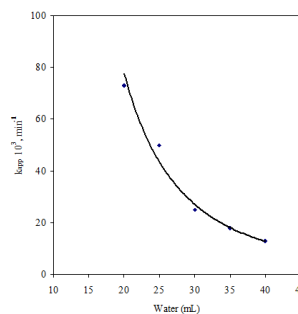
Figure: 1

Figure: 5

Caption of Tables

Table 1.
Effect of amount of Allyl bromide (AB) on the rate of O-allylation of

phenol under ultrasonic condition: 30g of KOH, 30 mL of H_2O, 0.2g of internal standard (Biphenyl), 0.0289 mol of allylbromide, 0.5 g of MPTC, 30 mL of chlorobenzene, 600 rpm, 45oC; ultrasound conditions (40 kHz, 300 W).

Table 2
Influence of ultrasonic frequencies on the rate of O-allylation of phenol: 0.0531mol of phenol, 30 g of KOH, 30 mL of H_2O, 0.2 of internal standard (Biphenyl), 0.0289 mol of allyl bromide, 0.5 g of MPTC, 30 mL of chlorobenzene , 600 rpm, 45oC; ultrasound conditions (40 kHz, 300 W).

Table 3
Influence of organic solvents on the rate of O-allylation 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 allyl bromide, 0.5 g of MPTC, 600 rpm, 45oC; ultrasound conditions (40 kHz, 300 W).

Table 4
Effect of various PTC's (5 mol % based on the limiting reagent, Allyl bromide) on the rate of O-allylation 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 allylbromide, 30 mL of chlorobenzene , 600 rpm, 45oC; under ultrasound conditions (40 kHz, 300 W).

Table 5
Influence of alkalinity on k_{app} in the O-allylation of phenol with allyl bromide catalyzed by MPTC under ultrasound condition; 0.0531mol of phenol, 0.2 g of internal standard (Biphenyl), 0.0289 mol of allyl bromide, 0.5 g of MPTC, 30 mL of chlorobenzene , 600 rpm, 45°C; ultrasound conditions (40 kHz, 300 W).

Table 1

Entry no.	Allyl bromide (AB) g	k_{app} x 103, min^{-1}
1.	2.5	30.8
2.	3.0	28.4
3.	3.5	25.6
4.	4.0	23.8
5.	4.5	18.9

Effect of amount of Allyl bromide (AB) on the rate of O-allylation of phenol under ultrasonic condition: 30g of KOH, 30 mL of H_2O, 0.2g of internal standard (Biphenyl), 0.0289 mol of allylbromide, 0.5 g of MPTC, 30 mL of chlorobenzene, 600 rpm, 45°C; ultrasound conditions (40 kHz, 300 W).

Table 2

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-allylation 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 allyl bromide, 0.5 g of MPTC, 30 mL of chlorobenzene , 600 rpm, 45°C; ultrasound conditions (40 kHz, 300 W).

Table 3

	Solvent				
	Cyclohexane	benzene	Toluene	Anisole	Chlorobenzene
Ea (Dielectric constant)	2.02	2.28	2.31	4.30	5.60

k_{app} x 10^3, min^{-1}	10.8	13.2	18.9	23.6	25.2

Influence of organic solvents on the rate of O-allylation 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 allyl bromide, 0.5 g of MPTC, 600 rpm, 45°C; ultrasound conditions (40 kHz, 300 W).

Table 4

Entry no.	PTC (50 mol %)	k_{app} x 10^3, min^{-1}
1.	MPTC	25.3
2.	TEAC	23.7
3.	TEAB	22.4
4.	BTEAC	20.6
5.	BTEAB	19.5
6.	TBAB	18.9

Effect of various PTC's (5 mol % based on the limiting reagent, Allyl bromide) on the rate of O-allylation 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 allylbromide, 30 mL of chlorobenzene , 600 rpm, 45°C; under ultrasound conditions (40 kHz, 300 W).

Table 5

Entry no.	Amount of KOH(g)	k_{app} x 10^3, min^{-1}
1.	20	16.2
2.	25	20.9
3.	30	25.4
4.	35	33.8
5.	40	42.3

Influence of alkalinity on k_{app} in the O-allylation of phenol with allyl bromide catalyzed by MPTC under ultrasound condition; 0.0531mol of phenol, 0.2 g of internal standard (Biphenyl), 0.0289 mol of allyl bromide, 0.5 g of MPTC, 30 mL of chlorobenzene , 600 rpm, 45°C; ultrasound conditions (40 kHz, 300 W).

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