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Fundamental analysis of microwave irradiated liquid–liquid phase transfer catalysis (MILL-PTC): Simultaneous measurement of rate and exchange equilibrium constants in selective *O*-alkylation of *p-tert*-butylphenol with benzyl chloride

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Abstract

Fundamentals of low power microwave irradiated liquid–liquid phase transfer catalysis (MILL-PTC) have been brought out in enhancements in the rates of alkylation of *p-tert*-butylphenol with benzyl chloride and selectivity towards *O*-alkylated product. Further, a method was proposed for measuring simultaneously the reaction rate constant and anion exchange equilibrium constant from the same set of data. The reaction was studied with a variety of phase transfer catalysts using conventional heating (CH) as well as low power (40 W) microwave irradiation (MW). The *O*-alkylated product 1-(1,1-dimethylethyl)-4-phenylmethoxybenzene was selectively formed with tetra-*n*-butylammonium bromide (TBAB) as the catalyst under both CH and MW conditions. The rates of PTC reaction were greatly accelerated under MW. The activation energy of the reaction under CH and MW was nearly the same but the pre-exponential factor in the Arrhenius equation was increased by orders of magnitude under MW. The Gibbs free energy calculated for the exchange reactions suggested that the entropy of MILL-PTC reaction was greater than that of conventionally heated liquid–liquid PTC reaction.
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Keywords: Microwave irradiated liquid–liquid phase transfer catalysis (MILL-PTC); Intensification of rates; Reaction kinetics; Modeling; *p-tert*-Butylphenol; Benzyl chloride; *O*-Alkylation; Rate constant; Equilibrium constant

1. Introduction

Substituted aromatic ethers are valuable as perfume and flavour compounds. Synthesis of such ethers is amenable to phase transfer catalysis (PTC) [1–3]. Ethers are synthesized by alkylation reactions using different catalysts such as phase transfer catalysts in two liquid phases [4] and in three liquid phases [5,6], cation-exchange resins [7], bases [8,9] and clays [10]. Isomerization is also used to make ethers [11]. The novelties of liquid–liquid (L–L) [12–14], solid–liquid (S–L) [15–17], solid–liquid–omega–liquid (S–L–ω–L) [18,19] and liquid–liquid–liquid (L–L–L) PTC [9,10,20] reactions have been conducted in our laboratory for reactions employed in perfumery, pharmaceutical and agrochemical industries including kinetic modeling. Of late, microwave irradiation has been increasingly used as a synthetic tool in a large number of studies. Microwave technology is a novel approach towards clean and green chemistry and it is a very convenient, safe and rapid methodology. The slow uptake of the technology has been attributed to its initial lack of controllability and reproducibility, coupled with a general lack of understanding of the basics of microwave dielectric heating [21]. The microwave-assisted organic synthesis (MAOS) technology has moved to the forefront of chemical research today and several reviews, monographs, books, etc. have appeared from all parts of the

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Nomenclature

$[A]_{org}$	concentration of benzyl chloride in the organic phase (mol/cm^3)
ΔG	Gibb's free energy (kcal/mol)
ΔH	enthalpy (kcal/mol)
k_{org}	second order rate constant of forward reaction in organic phase (cm^3/(mol s))
K_e	overall ion exchange reaction equilibrium constant
N_Q	total moles of catalyst added to the system at time $t = 0$ (mol)
$[N_Q]_{org}$	moles of the catalyst per unit volume of organic phase (mol/cm^3)
$[Q^+X^-]_{org}$	concentration of quaternary salt in the organic phase (mol/cm^3)
$[Q^+X^-]_{aq}$	concentration of quaternary salt in the aqueous phase (mol/cm^3)
$[RO^-Q^+]_{aq}$	concentration of nucleohile ion-pair in the aqueous phase (mol/cm^3)
$[RO^-Q^+]_{org}$	concentration of nucleohile ion-pair with quat in the organic phase (mol/cm^3)
ΔS	entropy (kcal/(mol K))
T	temperature (K)
V_{org}	volume of the organic phase (cm^3)
X^-	leaving group
X_A	fractional conversion of reactant A
Y^-	nucleophile

Greek symbols

ϕ	fraction of quaternary cation in the organic phase

world [22–30]. Microwave assisted heating has been shown to be an invaluable method, since it reduces the reaction times dramatically, typically from days or hours to minutes or seconds. When multi-mode power input at higher rates is used, it leads to evaporation of the solvent. A large number of papers, which appeared in several journals, are based on use of multi-mode domestic ovens with high power input, which have a serious drawback of non-reproducibility of results, since the intensity of energy supplied to the reaction mixture is a strong function of the position of the sample on the rotating platform in the oven. This fact was grossly overlooked, since several different types of reactions occurred in a short time, in some cases as solid–liquid or solid–solid reactions. However, scale-up of microwave assisted reactions has become a formidable task as has been brought out recently. Obviously, no kinetic studies have been reported and such data essential for scale-up are missing from published literature [24–26].

The rates of the PTC reactions can be synergistically enhanced by using microwave irradiation including selectivity of the desired product. The microwave irradiation (MW) assisted solid–liquid phase transfer catalyzed synthesis of *o*-ethoxyphenol has been reported [27]. The solid composite copper–copper chloride assisted alkylation of naphthols promoted by microwave irradiation has been developed [28]. Loupy et al. [29] have given a detailed account of the microwave activation in various solid–liquid phase transfer catalyzed reactions [30]. Several large pharmaceutical companies have reported dramatic productivity increases in switching from conventional synthesis to MAOS [30]. Organic syntheses of various ethers employing solid–liquid phase transfer catalyst under microwave conditions have been reported by quite a few researchers [31–36].

The literature published on microwave assisted PTC reactions so far deals with only S–L PTC at very high input energy (typically of the order of 600 W) which leads to a final temperature of over 140–180 °C depending on the polarity of the reaction medium. The solubility of the solid reagent increases substantially in the medium at these temperatures thereby masking the effect of the phase transfer catalyst. Furthermore, since most of the quaternary salts used, as catalysts are thermally unstable at high temperatures and at temperatures beyond 120–130 °C, they may become totally ineffective due to decomposition; for instance, in the presence of bases, the degradation will start from 60 °C onwards and is a strong function of concentration of the base [1]. The published literature is totally devoid of studies in kinetics of MW assisted PTC. One of the reasons is that the reaction times for small quantities of reagents using a multi-mode microwave irradiation range from a few seconds to a few minutes and sampling has been difficult. Secondly, the purpose of most of the studies was to demonstrate the versatility of MAOS in intensifying rates of reactions and selectivites, and the "greenness" of the technique. However, there is no report on microwave assisted L–L PTC reactions, which are typically conducted at milder temperatures less than 100 °C.

After studying these lacunae, we have been convinced that to study L–L PTC reaction of industrial importance under milder conditions would throw light on enhancement in rates and selectivities under microwave irradiation. Alkylation reactions are one of the most widely studied PTC reactions. Thus, the selectivity of *O*-alkylation over *C*-alkylation in reaction between *p-tert*-butylphenol and benzyl chloride was taken as a model reaction for low energy mono-mode microwave irradiation. The *O*-alkylated product 1-(1,1-dimethylethyl)-4-phenylmethoxybenzene is an important intermediate, which is specifically used in the preparation of heat resistant paper of improved sensitivity and stability. Thus, the current work has an academic impact and industrial applicability, demonstrating the prowess of low energy microwave irradiated liquid–liquid phase transfer catalysis (MILL-PTC). Further, a general modeling method is devised, which would enable us to determine the rate constant and also the overall equilibrium constant for exchange of anions, using the same set of data. The subtle differences in the two modes of heating are clearly due to differences in energy of activation and Gibbs free energy for the system.

2. Experimental

2.1. Materials

p-tert-Butylphenol was obtained from Sisco Research Laboratories Pvt. Ltd. Mumbai, India. All other reagents including benzyl chloride, toluene, diphenyl ether and sodium hydroxide, all of A.R. grade, were procured from M/s s.d. Fine Chemicals Pvt. Ltd. Mumbai. All phase transfer catalysts used in this work were received as gift samples from M/s Dishman Pharmaceuticals and Chemicals Ltd., Ahmedabad, India.

2.2. Experimental set-up

2.2.1. Conventionally heated reactor

The experimental set-up for reactions using conventional heating consisted of a 5.0 cm i.d. fully baffled mechanically agitated contactor of 100 mL total capacity equipped with a standard six-bladded turbine impeller and a reflux condenser. The reactor was kept in a thermostatic bath whose temperature could be maintained within ±1 °C of the desired value. Typical runs were conducted by taking 0.01 mol benzyl chloride, 2 mL diphenyl ether as an internal standard and the total volume was made up to 30 mL with toluene. The aqueous phase comprised of 0.01 mol *p-tert*-butylphenol and 0.012 mol NaOH dissolved in water to make up to 30 mL. Both the organic and aqueous phases were added to the reactor and 0.002 mol of catalyst was then added after the temperature had reached the set value. All the typical reactions were carried out at 90 °C and 1000 rpm.

2.2.2. Microwave reactor

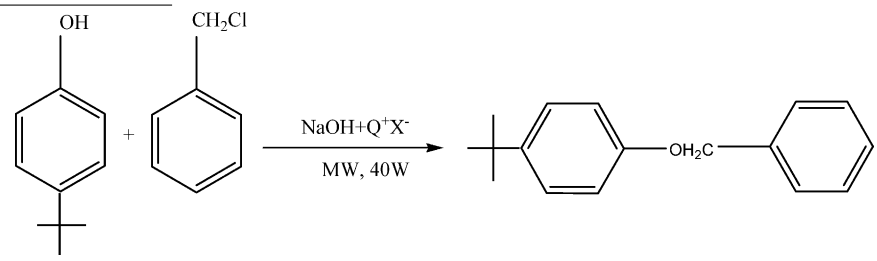
The experimental set-up for the microwave experiment was the commercially available "Discover" system of CEM Corporation, USA (Model CEM-SP 1245), with proper temperature and pressure feedback systems for complete control of the reaction conditions. It is a mono-mode microwave system. The reactor consisted of 3.5 cm i.d. fully baffled mechanically agitated reactor of 150 cm^3 capacity, which was equipped with four equispaced baffles and a six-bladed pitched-turbine impeller and a reflux condenser. The organic and aqueous phases comprised of the same composition as mentioned above for the conventional heating system. The reaction was allowed to reach the desired temperature and the initial/zero time sample was collected. The catalyst was then added. Typically runs were conducted at 90 °C and 1000 rpm. It is important to note here that the power supplied to the system, during the entire reaction, was below 40 W.

2.3. Analysis

Samples were withdrawn periodically in both the cases of the conventional heating and microwave radiation and GC analyses were performed (Chemito Model 8610) by using a stainless steel column (3.25 mm × 4 m) packed with 10% (w/w) OV-17/WHP. The quantification was done by calibration using synthetic mixtures. The products were also confirmed by GC–MS.

3. Results and discussion

3.1. Reaction



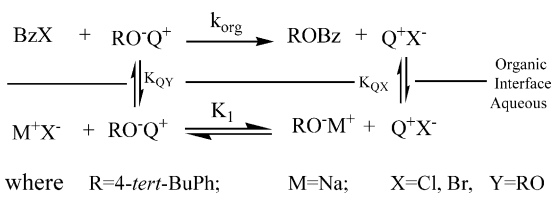
The above reaction shows only the *O*-alkylated product. However, the *C*-alkylated product, 2-benzyl-4-*tert*-butylphenol was also obtained with some catalysts in a few cases, which will be described later.

3.2. Proposed mechanism and rate equation

Almost any type of organic reactions requiring heating or thermal conditions can be performed using microwave irradiation. Microwave dielectric heating is dependent on the ability of the solvent or matrix to absorb microwave energy and convert into heat. When irradiated at microwave frequencies, the ions or dipole of the sample align in the applied electric field. As the applied field oscillates, the dipole or ion field tries to realign itself with the alternating electric field and, in the process, energy is lost in the form of heat through molecular friction and dielectric loss. The amount of heat generated is directly related to the ability of the matrix to align itself with the frequency of the applied field. If the dipole does not have time to realign, or it reorients too quickly with the applied field, no heating occurs. Microwave irradiation produces efficient in situ heating, resulting in even temperature throughout the sample, as compared with conventional heating. Microwave energy is applied too quickly (every 10^{-9} s) for molecules to completely align in the changing field (molecular relaxation rates are on the order of 10^{-5} s). As a result, the molecules in solution are constantly stimulated by microwave energy, without time to completely relax. Some molecules heat more rapidly in a microwave than

others on a basic level due to the polarity of the molecule. This can be measured as the dielectric loss, the amount of input microwave power that is lost as thermal energy.

The effect of conventional heating and microwave irradiation was studied at the same temperatures. According to the published literature, there is no change in the mechanism of the reaction, instead the enhancement in rates due to increased frequency of collision between the reactants. Yadav and Bisht [37] recently gave a detailed account of microwave irradiation in enhancing rates of solid–liquid PTC. There is no distribution of the catalyst in the case of S–L PTC and all catalyst resides in the organic phase, whereas there is a distribution of the catalyst between the aqueous and organic phases in L–L PTC. The following mechanism is discussed with reference to the general L–L PTC under conventional heating. In the case of low power MILL-PTC, the same mechanism is applicable with the symbols for the rate constant and equilibrium constants denoted by an additional subscript M.



p-tert-Butylphenol (ROH) was converted in the presence of an aqueous alkali into the corresponding phenate (RO^-M^+) salt in situ, and therefore no free ROH was present. The pH of the aqueous phase was always alkaline. The aqueous phase reaction produces the ion-pair (RO^-Q^+), which is instantaneously transferred to the organic phase due to high lipophilicity of the catalyst cation. It reacts with benzyl chloride (BzCl) to produce the ether ROBz in the organic phase and the regenerated catalyst Q^+X^- is transferred across the interface to the aqueous phase. The quaternary cation Q is distributed as four ion-pairs when the selectivity is 100% to *O*-alkylation. The ion exchange equilibria across the interface can be expressed in terms of an overall exchange reaction equilibrium constant (K_e), which is also called selectivity equilibrium constant, for exchange of $[X^-]_{aq}$ by $[Y^-]_{aq}$ and its transfer to the organic phase, by the following equation:

$$[Q^+X^-]_{org} + [Y^-]_{aq} \overset{K_e}{\longleftrightarrow} [Q^+Y^-]_{org} + [X^-]_{aq} \tag{1}$$

$$K_e = \frac{[Q^+Y^-]_{org}}{[Q^+X^-]_{org}} \times \frac{[X^-]_{aq}}{[Y^-]_{aq}} \tag{2}$$

The individual ion-pair distribution constants between organic and aqueous phases and their relationship with K_e and K_1 are given by:

$$K_{QX} = \frac{[Q^+X^-]_{org}}{[Q^+X^-]_{aq}}, \qquad K_{QY} = \frac{[Q^+Y^-]_{org}}{[Q^+Y^-]_{aq}},$$

$$K_e = \frac{K_{QY}[Q^+Y^-]_{aq}}{K_{QX}[Q^+X^-]_{aq}} \times \frac{[X^-]_{aq}}{[Y^-]_{aq}} = \frac{K_{QY}}{K_{QX}} K_1 \tag{3}$$

$$K_e \frac{K_{QX}}{K_{QY}} = \frac{[Q^+Y^-]_{aq}}{[Q^+X^-]_{aq}} \frac{[X^-]_{aq}}{[Y^-]_{aq}} = K_1 \tag{4}$$

Eq. (4) represents the equilibrium constant for the ion-pair exchange reaction in the aqueous phase.

If the overall reaction rate is controlled by the reaction in the organic phase, then the rate of reaction of benzyl chloride (A) in the organic phase is given by:

$$\frac{-d[A]_{org}}{dt} = k_{org}[A]_{org}[Q^+Y^-]_{org} \tag{5}$$

The concentration of the active catalyst in the organic phase needs to be substituted in terms of known concentrations.

$$[Q^+Y^-]_{org} = \frac{K_e[Q^+X^-]_{org}[Y^-]_{aq}}{[X^-]_{aq}} \tag{6}$$

The catalyst is distributed as two ions pairs in each of the organic and aqueous phases. If N_Q is total amount of catalyst (mol) added to the reaction mixture initially and ϕ is the fraction of the catalyst cation Q^+ distributed in the organic (reaction) phase, then:

$$[Q^+X^-]_{org}V_{org} + [Q^+Y^-]_{org}V_{org} = \phi N_Q \quad \text{(organic phase)} \tag{7}$$

$$[Q^+X^-]_{aq}V_{aq} + [Q^+Y^-]_{aq}V_{aq} = (1-\phi)N_Q \quad \text{(aqueous phase)} \tag{8}$$

From Eq. (7),

$$[Q^+Y^-]_{org} = \phi\frac{N_Q}{V_{org}} - [Q^+X^-]_{org} \tag{9}$$

Defining,

$$[N_Q]_{org} = \frac{N_Q}{V_{org}} = \text{total catalyst mol/unit organic phase volume} \tag{10}$$

Eq. (9) is converted to the following:

$$[Q^+Y^-]_{org} = \frac{\phi[N_Q]_{org}}{\left(1 + \frac{1}{K_e}\frac{[X^-]_{aq}}{[Y^-]_{aq}}\right)} \tag{11}$$

Eq. (5) is rewritten with the help of Eq. (11) as:

$$\frac{-d[A]_{org}}{dt} = k_{org}[A]_{org}\frac{\phi[N_Q]_{org}}{\left(1 + \frac{1}{K_e}\frac{[X^-]_{aq}}{[Y^-]_{aq}}\right)} \tag{12}$$

and the concentrations terms $[A]_{org}$, $[X^-]_{aq}$ and $[Y^-]_{aq}$ can be substituted in terms of X_A, the fractional conversion of A. For equimolar concentrations of the reactants the rate equation is:

$$\frac{dX_A}{dt} = k_{org}\frac{\phi[N_Q]_{org}(1-X_A)}{\left(1 + \frac{1}{K_e}\frac{X_A}{(1-X_A)}\right)} \tag{13}$$

After separation of variables and integration, Eq. (13) leads to:

$$\ln(1-X_A)[1-K_e] + \frac{X_A}{(1-X_A)} = K_e k_{org}\phi[N_Q]_{org}t \quad (14)$$

It is possible to determine the rate constant (k_{org}) and the equilibrium constant (K_e) by further manipulation of Eq. (14) as given below:

$$\frac{X_A}{(1-X_A)\ln(1-X_A)} = K_e k_{org}\phi[N_Q]_{org}\frac{t}{\ln(1-X_A)} + [K_e - 1] \quad (15)$$

Eq. (15) is that of a straight line. When $\frac{X_A}{(1-X_A)\ln(1-X_A)}$ is plotted against $\frac{t}{\ln(1-X_A)}$, it should give a slope of $K_e k_{org}\phi[N_Q]_{org}$ (time^{-1}) and intercept of $[K_e - 1]$ from which the equilibrium constant K_e and the rate constant $k' = k_{org}\phi$ are obtained.

To evaluate the value of ϕ independent experiments were performed both under conventional heating (CH) and MW heating using TBAB as the catalyst. Both the reactions were performed by taking the reactants as had been the case with the standard reaction, the only difference being the absence of benzyl chloride reactant. The value of ϕ was found to be 0.883 and 0.885 for CH and MW heating, respectively, which also demonstrates that the quaternary cation is mostly distributed in the organic phase for L–L PTC with high molecular weight catalysts. This indicates that the distribution constant is almost constant and is independent of the microwaves. For further calculation the average value of ϕ was taken as 0.884.

The microwaves irradiation can affect both the reaction rate constant and equilibrium constant, which will be reflected in conversion and selectivity, without affecting the basic reaction mechanism.

4. 4. Validation of the model

In order to verify the proposed mechanism of the reaction and validate the model, the effects of various parameters on the rates of the reaction and selectivity were studied both for conventional heating and microwave irradiation at a precisely controlled temperature of 90 °C in each case. With a 40 W power input a temperature of 90 °C could be precisely maintained.

4.1. Effect of different catalysts

Various catalysts such as tetra-*n*-butylammonium bromide (TBAB), tetra-*n*-propylammonium bromide (TPAB), tetra-*n*-butylammonium iodide (TBAI), ethyltriphenylphosphonium bromide (ETPB) and tetraethylammonium bromide (TEAB) were employed under otherwise similar experimental conditions for conventional heating and microwave irradiation. The reaction was also carried out in the absence of catalyst (Fig. 1). The selectivity of the *O*-alkylated product after 3 h is given in parentheses in each caption under the same figure.

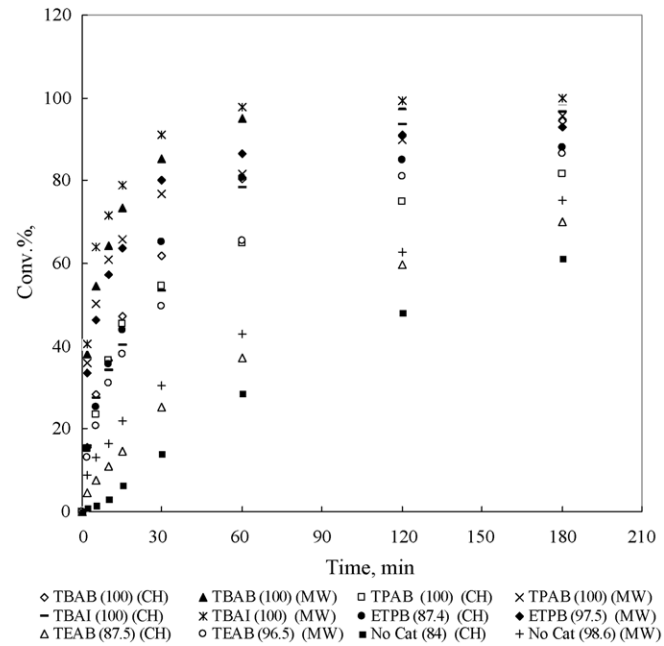


Fig. 1. Effect of different catalysts on conversion and selectivity under conventional heating (CH) and microwave irradiation. The numbers in parentheses show percent selectivity; *p-tert*-butylphenol 0.01 mol, NaOH 0.012 mol, benzyl chloride 0.01 mol, diphenyl ether (internal standard) 2.0 mL, toluene 30 mL, water 30 mL, catalyst 0.002 mol, temperature 90 °C, speed 1000 rpm.

The enhancement factors based on initial rate of reaction in the presence the catalysts at 90 °C and 1000 rpm with reference to no-catalyst using conventional heating were in the following order for both conventionally heated L–L PTC (CH) and microwave irradiated L–L PTC (MILL-PTC). There was resistance to the transfer of the ion-pairs across the interface, which will be discussed later.

Conventional heating activities: No catalyst (1) < TEAB (4.8) < TBAB (15.6) < ETPB (18.8) < T PAB (19) < TBAI (21.9)
Microwave irradiation activities: No catalyst (9.8) < TEAB (15.6) < TBAB (41.9) < ETPB (40.6) < TPAB (42.5) < TBAI (53.1)

It should be noted that the reaction without any catalyst but conventional heating was sluggish and only 0.8% conversion was obtained within 2 min. There was apparently no change in the order of the catalyst activity for both the cases of CH and MW, except TBAB and ETPB, which were nearly equally effective. However, with TBAB, the selectivity at the end of the reaction was 100%. TEAB resided more in aqueous phase than in organic phase. ETPB did not give complete selectivity, which was also the case with TEAB. TEAB was mainly partitioned in the aqueous phase and hence was ineffective. It is clear that there was rate intensification by a factor of 3 with 100% selectivity with MILL-PTC for TBAB. Besides, TBAB

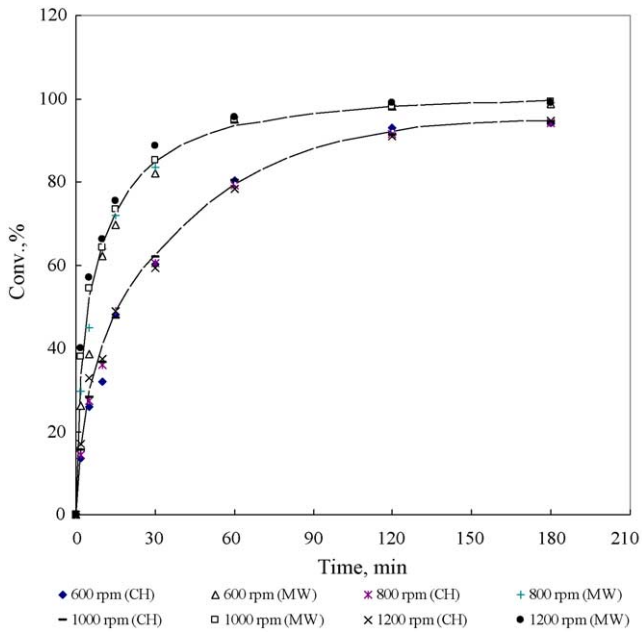


Fig. 2. Effect of speed of agitation on conversion for CH and MILL-PTC; *p-tert*-butylphenol 0.01 mol, NaOH 0.012 mol, benzyl chloride 0.01 mol, diphenyl ether (I.S.) 2.0 mL, toluene 30 mL, water 30 mL, TBAB 0.002 mol, temperature 90 °C, time 3 h.

is a cheaper and readily available catalyst. Hence, TBAB was chosen as the catalyst for all further experiments.

4.2. Effect of speed of agitation

To ascertain the influence of mass transfer resistance, the speed of agitation was varied in the range of 500–1200 rev/min under otherwise similar conditions in the presence of TBAB (Fig. 2). The enhancement in the reaction rates is clearly visible for MILL-PTC vis-à-vis conventional heating. The conversions were found to be practically the same at 800 and 1200 rpm, which suggested that the reaction was free of mass transfer influence. Therefore, further experiments were carried out at 1000 rpm in both modes of heating.

4.3. Effect of catalyst (TBAB) concentration

TBAB concentration was varied from 3.3×10^{-5} to 1.67×10^{-4} mol/cm^3 of the organic phase (Fig. 3). With increasing catalyst concentration, there is an increase in the conversion, which are the characteristics of a PTC reaction. Fig. 4 shows the plots of initial rate for various catalyst concentrations, which are linear in both the cases. As expected there is an enhancement in reaction rate under the influence of microwaves. The model was tested by invoking Eq. (15) and the pertinent variables are plotted in Fig. 5 for the control experiment with a catalyst concentration, $[N_Q]_{org}$, of 6.7×10^{-5} mol/cm^3 for both CH and MW. The model gives a very good fit. The values of k_{org} and K_e were calculated from the slope and intercept as 648.0 cm^3 mol^{-1} s^{-1} and 1.33 for CH, whereas k_{org-M} and K_e were calculated at 1619.0 cm^3 mol^{-1} s^{-1} and 1.54 for MW at 90 °C, respectively. It is obvious that the microwave irradiation has enhanced the rate of reaction by a factor of 3 and there is also a marginal increase in K_e. It was interesting to note that the values of K_e for exchange between two anions for a number of cases are in the range of 0.9–3.1 for different solvents and for toluene as a solvent it is in the range of 1.2–1.5 for commonly used nucleophiles and leaving anions under

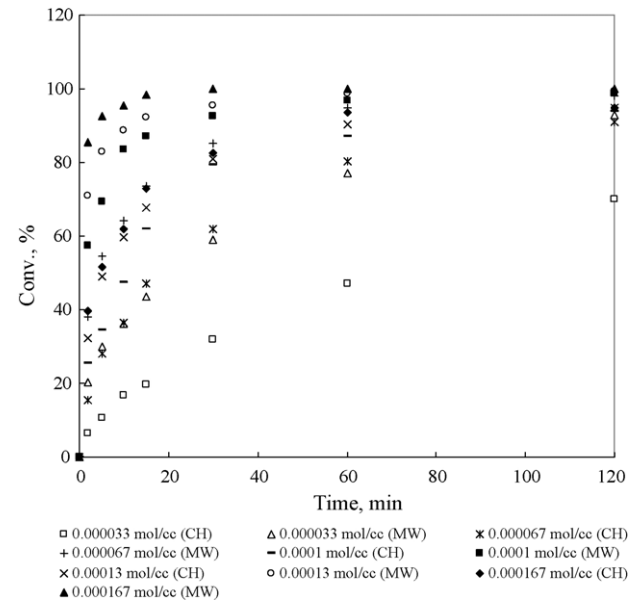


Fig. 3. Effect of catalyst (TBAB) concentration on conversion under CH and MW; *p-tert*-butylphenol 0.01 mol, NaOH 0.012 mol, benzyl chloride 0.01 mol, diphenyl ether (I.S.) 2.0 mL, toluene 30 mL, water 30 mL, temperature 90 °C, speed 1000 rpm.

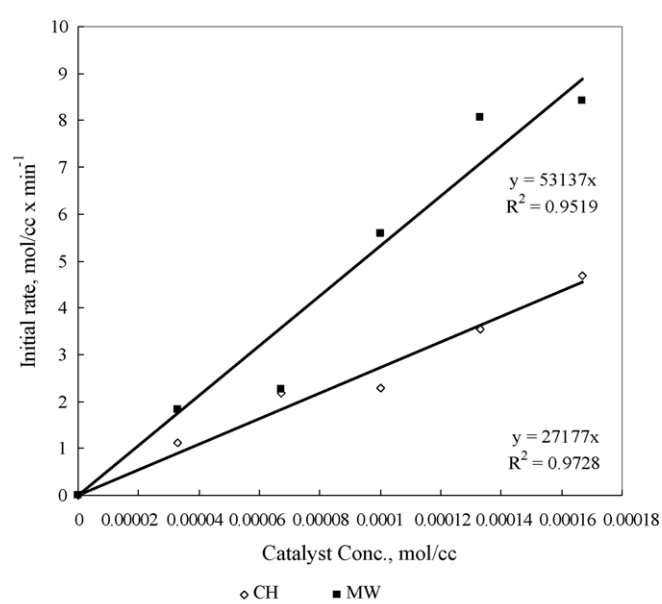


Fig. 4. Plot of initial rate vs. catalyst concentration.

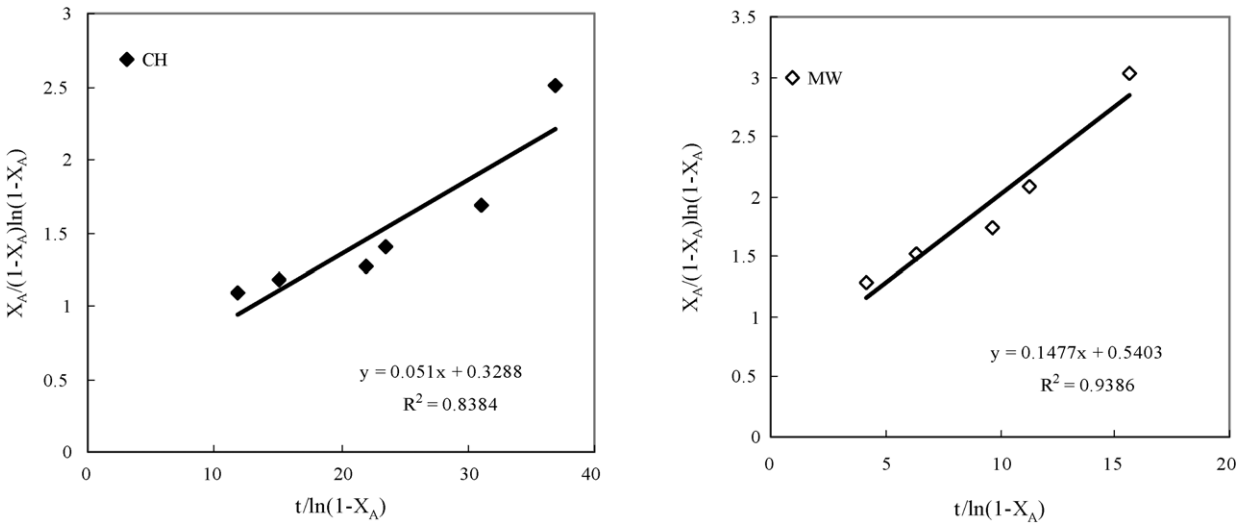


Fig. 5. Evaluation of rate constant and exchange reaction equilibrium kinetic plot for effect of catalyst (TBAB) concentration (6.7×10^{-4} mol/cm^3); $k_{org} = 648.0$ cm^3 mol^{-1} s^{-1}; $k_e = 1.3288$ for CH L–L PTC; $k_{org-M} = 1619.0$ cm^3 mol^{-1} s^{-1}; $K_{e-M} = 1.5403$ for MILL-PTC (p.s. in order to bring the plot in first quadrant, Eq. (15) was multiplied by −1 throughout).

conventional heating. This suggests that our method of evaluating both the rate constant and equilibrium constant is indeed sound. The utility of this method was tested in all further studies and only a few cases are reported as illustrations.

4.4. Effect of phase volume ratio

The effect of volume ratio of aqueous phase to organic phase was studied for 1:0.5, 1:1 and 1:1.5 ratios under otherwise similar conditions for both conventional and microwave heating. The moles of all reactants and catalyst added were also kept constant (Fig. 6). When the phase volume ratio was taken as 1:0.5 the conversion was higher than that for 1:1 phase ratio. This is attributed to higher concentration of the substrate in the organic phase, which leads to higher reaction rate. This pattern remained the same when reaction was conducted under microwave heating. The model was tested (Fig. 7) for 1:1.5 (aqueous:organic) ratio as an example for both CH and MW.

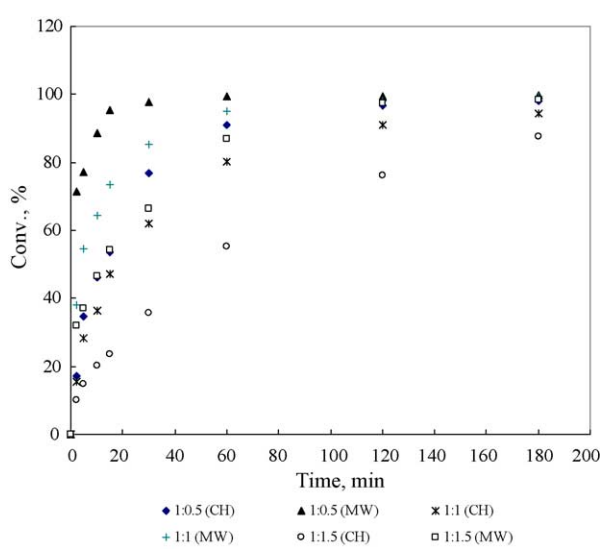


Fig. 6. Effect of phase volume ratio (aqueous: organic); *p-tert*-butylphenol 0.01 mol, NaOH 0.012 mol, benzyl chloride 0.01 mol, diphenyl ether (I.S.) 2.0 mL, TBAB 0.002 mol, temperature 90 °C, speed 1000 rpm, time 3 h.

4.5. Effect of benzyl chloride concentration

The concentration of benzyl chloride was varied from 1.67×10^{-4} to 3.3×10^{-4} mol/cm^3 under otherwise similar conditions (Fig. 8). The reaction was carried out both with conventional and microwave heating. The initial rate of reaction increased linearly with benzyl chloride concentration for both the cases. As an illustration the model fitting is shown in Fig. 9 for benzyl chloride concentration of 2.5×10^{-4} mol/cm^3.

4.6. Effect of NaOH concentration

Fig. 10 shows the effect of NaOH concentration over a range of 3.3×10^{-4} to 6.7×10^{-4} mol/cm^3 on the conversion of benzyl chloride. In these experiments equimolar quantities of *p-tert*-butylphenol and benzyl chloride (0.01 mol each) were used and mole ratio of NaOH to *p-tert*-butylphenol was varied at 1:1, 1.2:1, 1.5:1 and 2:1 which correspond to 3.3×10^{-4}, 4×10^{-4}, 5×10^{-4} and 6.7×10^{-4} mol/cm^3, respectively. The initial rates were the same and the conversions up to 40% were practically the same at the same duration of time. However, beyond this the conversions with higher molar ratio were marginally higher. This pattern was observed even when the reaction was carried out under microwave heating. This is due to the fact that the K_e values are affected by ionic strength of the aqueous phase and also entire ROH is converted into Q^+OR^- ion-pairs when the mole ratio of NaOH

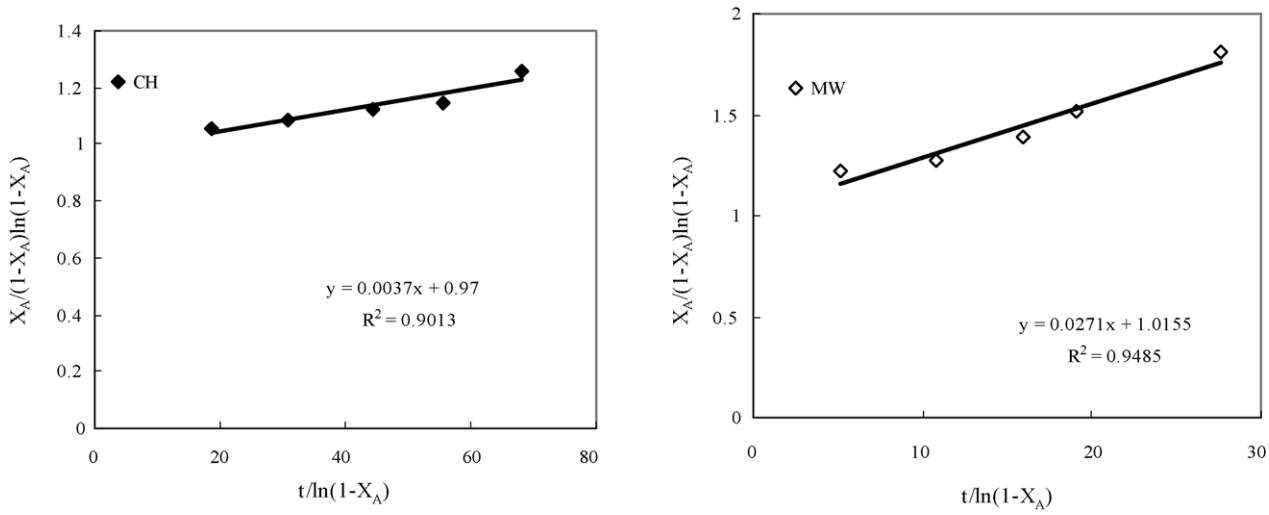


Fig. 7. Kinetic plot for effect of phase volume ratio (aqueous:organic = 1:1.5) (p.s. in order to bring the plot in first quadrant, Eq. (15) was multiplied by −1 throughout).

to *p-tert*-butylphenol is greater than one. But at the same time there is not much difference in conversions when a mole ratio of NaOH to *p-tert*-butylphenol of 1.2:1 ensures complete conversion of the phenol into sodium salt. Thus, to ensure complete conversion of *p-tert*-butylphenol to its sodium salt, 1.2 mol of NaOH per mol *p-tert*-butylphenol was taken for all the reactions.

4.7. Effect of temperature

The effect of temperature on the rate of reaction of benzyl chloride was studied in the range of 60–90 °C under otherwise similar reaction conditions. It was found that the overall conversion as well as the rate of reaction was higher under microwave irradiation vis-à-vis the conventional heating as depicted in Fig. 11. Likewise plots were made for all other temperatures and the values of k' and K_e were found and used in both the cases to estimate the activation energy (Fig. 12) and Gibb's free energy for the overall exchange reaction across the interface ($\Delta G = -RT \ln K_e$) (Fig. 13).

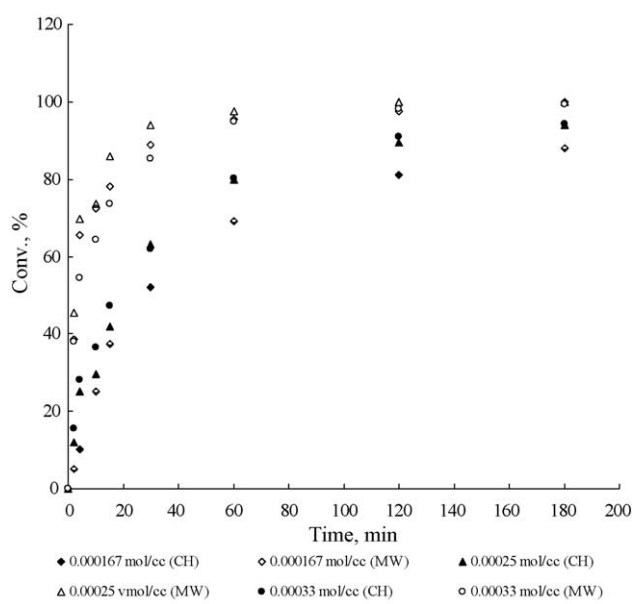


Fig. 8. Effect of benzyl chloride concentration; *p-tert*-butylphenol 0.01 mol, NaOH 0.012 mol, diphenyl ether (I.S.) 2.0 mL, toluene 30 mL, water 30 mL, TBAB 0.002 mol, temperature 90 °C, speed 1000 rpm, time 3 h.

The energy of activation was been found out to be 25.30 and 25.15 kcal/mol for conventional heating and microwave heating, respectively, which are very close. In microwave kinetics, neither does the overall order of reaction change nor does the order in individual reactants and catalyst concentration. Thus, the reaction rate is enhanced due to increased rate constant. The rate constant can be written in the usual Arrhenius equation with activation energy and pre-exponential factor k_0. The activation energy values are practically the same in both types of heating. So only the parameter that can change is k_0. There has been some speculation that microwaves affect the orientation of molecular collisions and the activation energy, but there is no evidence that supports either of these ideas. Microwaves do not influence the orientation of those collisions, nor the activation energy. Activation energies remain constant for each particular reaction. However, microwave energy will affect the temperature parameter in this equation. An increase in temperature causes molecules to move about more rapidly, which leads to a greater number of more energetic collisions. This occurs much faster with microwave energy, due to the high instantaneous heating of the substance(s) above the normal bulk temperature, and is the primary factor for the observed rate enhancements [26].

The Gibbs free energy, ΔG_{CH} and ΔG_{MW}, was calculated for the overall exchange reaction at −1.68 and −3.52 kcal/mol for conventional heating and microwave heating, respectively. ($\Delta G = \Delta H - T\Delta S = -RT \ln K_e$). Negative values for both show that the overall exchange reaction is thermodynamically possible. ΔG_{MW} also shows that the

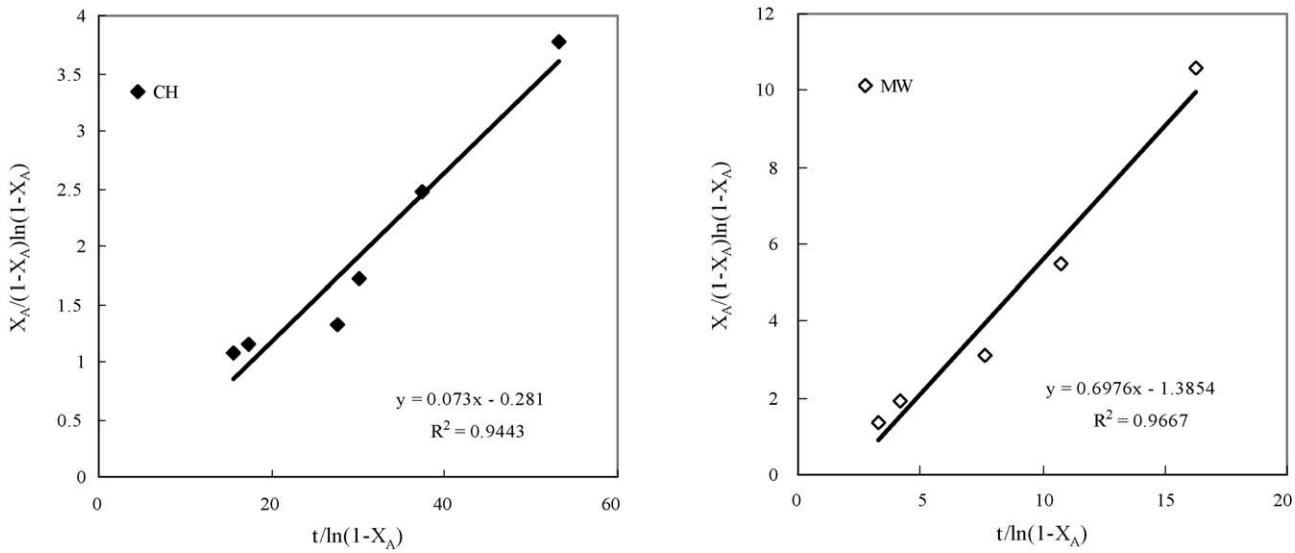


Fig. 9. Kinetic plot for effect of benzyl chloride concentration (0.00025 mol/cc) (p.s. in order to bring the plot in first quadrant, Eq. (15) was multiplied by −1 throughout).

entropy of MW reactions has increased due to more chaotic motion of molecules, which results in greater negative value for the exchange reaction.

4.8. Optimum conditions

The optimum conditions are as follows:

Molar ratio of NaOH to *p-tert*-butylphenol: 1.2.
Concentration of *p-tert*-butylphenol in toluene: 3.33×10^{-4} mol/cm^3.
Concentration of aqueous sodium hydroxide: 3.33×10^{-4} mol/cm^3.
Concentration of TBAB added in organic phase: 6.7×10^{-5} mol/cm^3.
Microwave irradiation power input: 40 W, temperature: 90 °C.
Tip speed of impeller: 100 cm/s.
Conversion of limiting reactant: 100%, yield = 100%, isolated yield = +95%.
Reaction time: 1 h.

After completion of the reaction, the reaction mixture was cooled and allowed to separate into two distinct phases. The organic phase was separated and washed with water and dried over sodium sulfate. The dried organic phase was subjected

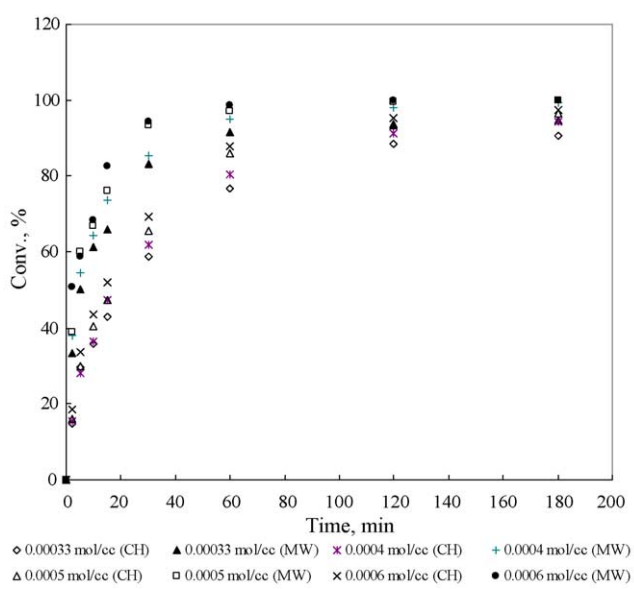


Fig. 10. Effect of NaOH concentration; *p-tert*-butylphenol 0.01 mol, benzyl chloride 0.01 mol, diphenyl ether (I.S.) 2.0 mL, toluene 30 mL, water 30 mL, TBAB 0.002 mol, temperature 90 °C, speed 1000 rpm, time 3 h.

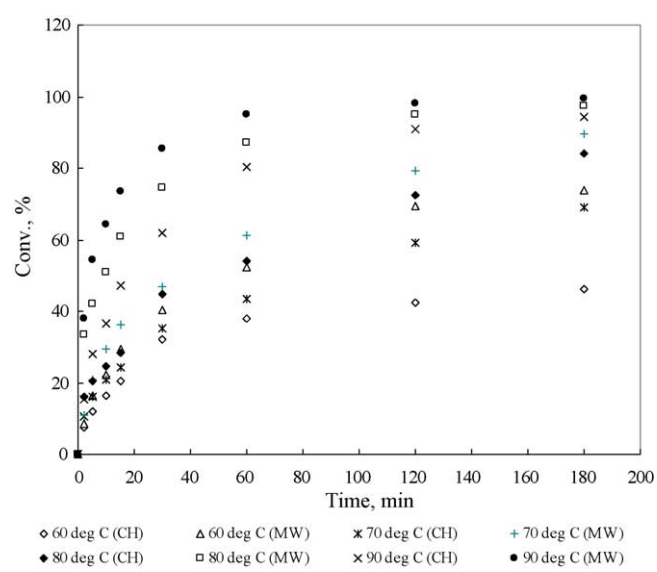


Fig. 11. Effect of temperature; *p-tert*-butylphenol 0.01 mol, NaOH 0.012 mol, benzyl chloride 0.01 mol, diphenyl ether (I.S.) 2.0 mL, toluene 30 mL, water 30 mL, TBAB 0.002 mol, speed 1000 rpm, time 3 h.

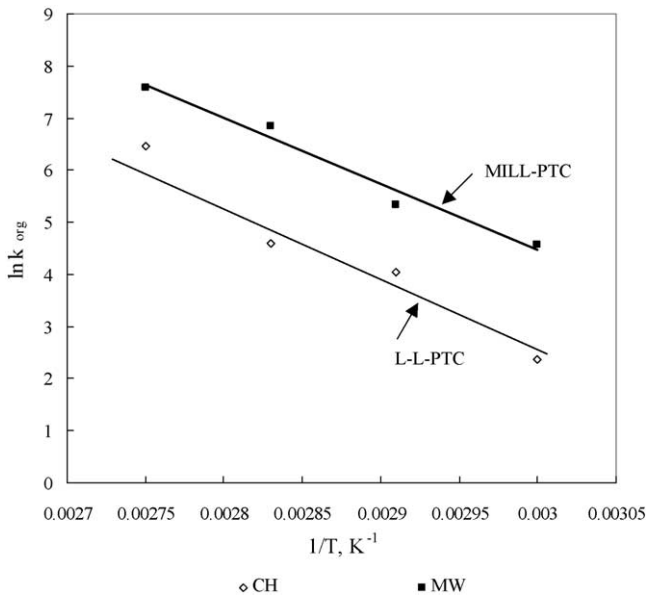


Fig. 12. Arrhenius plot.

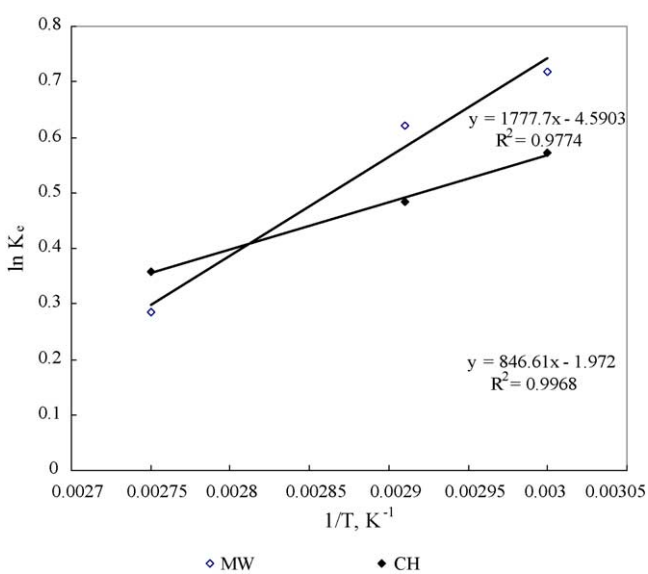


Fig. 13. Gibbs free energy plot for overall exchange reaction.

to vacuum distillation to give a semi-solid, which was further treated with methanol and recrystallised to give the product 1-(1,1-dimethylethyl)-4-phenylmethoxybenzene. Its melting point was found to be 64 °C, which matched with the literature value [38].

5. Conclusion

The novelties of synergistic combination of microwave irradiated phase transfer catalyzed etherification, of *p-tert*-butylphenol with benzyl chloride, was studied in detail in a biphasic L–L PTC system with TBAB as the catalyst. The low power input L–L PTC gave a true synergism between PTC and microwaves. Among all catalysts TBAB was found to be the best catalyst with 100% selectivity towards the ether under microwave heating. A complete theoretical analysis of the reaction was done for the first time to develop a model, which enabled us to calculate the rate constant and overall ion exchange reaction equilibrium constant from the same set of data. It provides excellent insight into MILL-PTC. The model was validated for both conventional and microwave irradiated L–L PTC. Microwaves do not influence the orientation of those collisions, nor the activation energy. Activation energies remained constant for the reaction. Microwave energy will affect the temperature parameter in the Arrhenius equation. An increase in temperature causes molecules to move about more rapidly, which leads to a greater number of more energetic collisions. This occurs much faster with microwave energy, due to the high instantaneous heating of the substance(s) above the normal bulk temperature, and is the primary factor for the observed rate enhancements. The Gibbs free energy could also be calculated for the exchange reaction for both conventional and microwave irradiation. In summary, the work provides an insight into the mechanism of microwave-assisted reactions.

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