

## An Efficient Ultrasound Promoted Single Spot Synthesis of P-Nitrophenyl Alkyl Ethers Under Solid-Liquid Multi-Site Phase-Transfer Catalysis Condition

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**Abstract:** The preparation of 1-isopropoxy-4-nitrobenzene from the reaction of 1-chloro-4-nitrobenzene (CNB) and isopropyl alcohol was carried out successfully using potassium hydroxide and catalyzed by a multi-site phase-transfer catalyst (MPTC) viz., 1,4-dibenzyl-1,4-diazoniabicyclo[2.2.2]octanium dichloride in a solid-liquid phase-transfer catalysis condition (SL-PTC) under low frequency ultrasound (40 kHz, 300W). Trace of water was added to the reaction system to enhance the rate of the reaction. The advantage of using SL-PTC is to avoid a serious hydration of potassium salt of isopropyl alcohol and the active intermediate. The reaction is greatly enhanced in the solid-liquid system, catalyzed by dual-site quaternary ammonium salt (MPTC) along with ultrasound irradiation (40 kHz, 300W). A pseudo first-order rate law is sufficient to describe the results, such as the effects of agitation speed, kind of phase transfer catalysts and the amount of MPTC, the effect of temperature, the volume of water, the concentration of 1-chloro-4-nitrobenzene (CNB), various alcohols, potassium hydroxide concentrations, on the conversion of 1-chloro-4-nitrobenzene. Alternative method of reactions was also carried out to get the same ether products.

**Keywords :** Multi-site phase-transfer catalyst; sonocatalysis; 4-nitrophenyl alkyl ethers; isopropyl alcohol; 1-chloro-4-nitrobenzene; alkyl bromides; 4-nitrophenol.

### 1. Introduction

Phase transfer catalysis (PTC) has been recognized as an effective practical methodology for organic synthesis due to its operational simplicity, mild reaction conditions, safety considerations and environmental concerns. Because of these salient features, the research and the developments of novel PTC especially to carry out the rare organic reactions have received considerable industrial interest<sup>1-4</sup>. Phase-transfer catalysts, such as quaternary ammonium and phosphonium salts, crown ethers, polyethylene glycols and cryptands, have been used to carry out the reactions between reactants which exist in the same or different phase(s)<sup>5-10</sup>. Presently, PTC has extensively been applied in the synthesis of organic chemicals via condensation<sup>11</sup>, substitution<sup>12</sup>, oxidation<sup>13</sup>, elimination<sup>14</sup> and polymerization<sup>15</sup> etc.

The application of ultrasound irradiation in organic synthesis has been broadly extended in recent years. The ultrasound has been used nowadays in both heterogeneous and homogenous reactions and it is considered as an environmentally benign alternative. In heterogeneous biphasic reactions, the most probably used phenomena are "cavitations" that results in the generation of high temperature and pressure at the centre of the collapsing bubble<sup>16</sup>. Cavitational collapse occurs at many locations in the reactor and creates different chemical environment i.e. chemical and physical effects which are strongly contribute in the process intensification. The physical effects favor the mass-transfer and chemical effects such as generation of hot spots and reactive species such as free radicals, which intensifies the chemical process limited by intrinsic chemical kinetics.

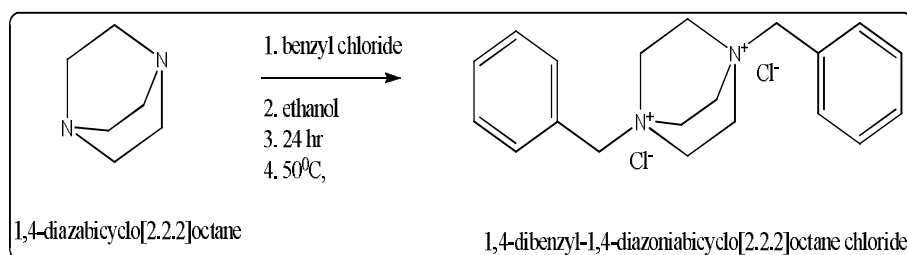
In heterogeneous reactions, the enhanced reactions occurred due to the mechanical effects of cavitations resulted in the enhanced mass-transfer rate by better contact between the different phases forming the fine emulsions. In general, while using ultrasound in the reactions that resulted in (i) increased yield, (ii) reduction of reaction time, (iii) increased conversion, (iv) reduction of by products formation and (v) increased selectivity towards desired product formation<sup>17</sup>. Recently reported studies reveal that ultrasound techniques combined with PTC are proved to be a useful technique in heterogeneous reactions<sup>18,19</sup>.

The multi-site phase-transfer catalyst is used in order to enhance the reaction rate and minimize the need of single-site PT catalyst in large amount and time consumption. The merit of MPTC is, it transfers more number of anionic species from aqueous phase to organic phase per cycle in contrast with single-site phase-transfer catalyst which transport single anionic species per cycle and has potential to be used in the solid-liquid system<sup>20,21</sup>. The ultrasound combined with MPTC shows significant enhancement in the rate<sup>22,23</sup>.

In this research work, we synthesized the series of 4-nitrophenyl alkyl ethers from two different path ways, (i) first one is, reacting the different alcohols with 1-chloro-4-nitrobenzene (ii) the other way is, reacting the different alkyl halides with 4-nitrophenol. The kinetic experiments were carried out for the reaction of isopropanol with 1-chloro-4-nitrobenzene under the effect of both ultrasound (40 kHz, 300 W) and multi-site phase-transfer catalyst viz., 1,4-dibenzyl-1,4-diazoniabicyclo[2.2.2]octanium dichloride (MPTC- scheme 1) which was prepared according to our previous report<sup>22(c)</sup> and here reported as a efficient catalysts for these etherification reactions.

### Scheme 1

#### Preparation of MPTC



## 2. Experimental

### 2.1. Chemicals, catalysts and solvents

All the reagents, including, DABCO (1,4-diazabicyclo[2.2.2]octane), isopropyl alcohol, propanol, butanol, pentanol, hexanol, octanol, 1-chloro-4-nitrobenzene (CNB), 4-nitrophenol, propyl bromide, butyl bromide, isopropyl chloride, pentyl bromide, hexyl bromide, octyl bromide, benzyl chloride, biphenyl, tetrabutylammonium bromide (TBAB), tetraethylammonium bromide (TEAB), tetrahexylammonium bromide (THAB), tetraoctylammonium bromide (TOAB), potassium hydroxide, potassium carbonate, n-hexane, toluene, chlorobenzene, p-xylene, dibutyl ether and other reagents for synthesis were guaranteed grade (GR) chemicals and were used without further purification.

### 2.2. Instrumentation

<sup>1</sup>H NMR and <sup>13</sup>C spectra were recorded on a Bruker 300 MHz and 75 MHz respective using TMS as an internal standard. Gas chromatography was carried out using a GC-Varian 3700 model. Ultrasonic water bath, Equitron, Media Instrument Manufacturing Company, Chennai, India-600 004. The ultrasonic generator was a thermostatic bath equipped with dual frequencies (28/40 kHz) and electric power 300 W with 0.0126 W/mL of power density and well discussed about the ultrasound process equipment in our previous report<sup>22 (a)</sup>. In this research work we used the 40 kHz, 300 W only for all the kinetic variations.

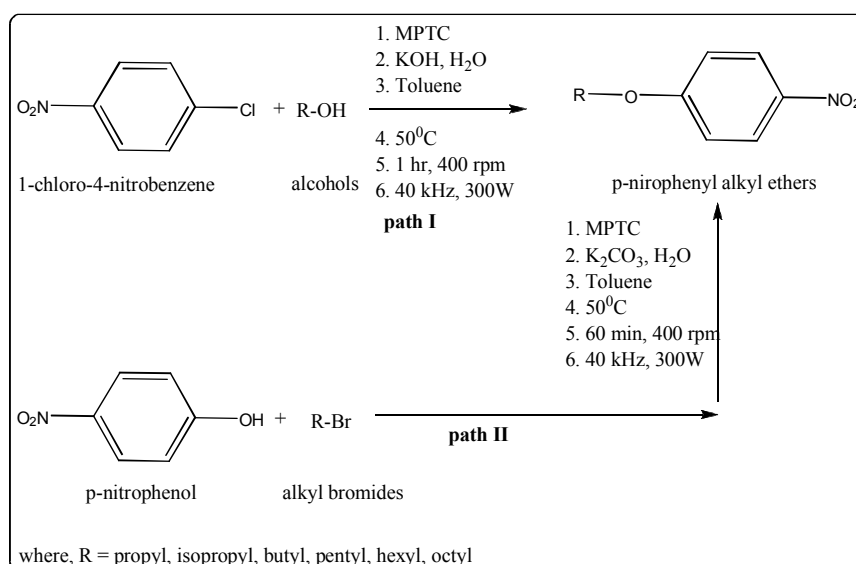
## 6. Kinetics of etherification reactions

The reaction was conducted on a 250 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 supported

at the centre of the sonicator. Known quantities of toluene (30 mL, solvent), potassium hydroxide (10 g) and 0.2 g biphenyl (IS-internal standard) were introduced into the reactor. Then, 10 mL of isopropyl alcohol and 1 g of 1-chloro-4-nitrobenzene (6.35 mmol), 3 mol % of the newly synthesized MPTC were introduced to the reactor to start the reaction. The reaction mixture was stirred at 400 rpm. The phase separation was almost immediate on arresting the stirring process. Samples were collected from the organic layer at 10, 20, 30, 40, 50 and 60 minutes into the 10 mL vials and pinch of anhydrous sodium sulphate was placed in the sample vials to absorb any moisture present in the organic layer. The kinetics was followed by estimating the amount of 1-chloro-4-nitrobenzene (limiting reagent) that disappeared and measured by 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<sup>0</sup>C; FID detector (300<sup>0</sup>C). Yields were determined from standard curve using biphenyl as an internal standard. The general reactions scheme is represented below for the etherification reactions (Scheme 2).

## Scheme 2

### Preparation of 4-nitrophenyl alkyl ethers



## 8. Results and discussion

The kinetic experiments of etherification were carried out under pseudo first order conditions, taking excess of alcohols and potassium hydroxide under the combined effect of sonication (40 kHz, 300W) and MPTC. The  $k_{app}$  value was obtained by plotting  $-\ln(1-X)$  versus time.

### 8.1. Effects of different stirring speeds

The reaction was carried out at different speed of agitation from 0 to 500 rpm with multi-site phase-transfer catalyst (1,4-dibenzyl-1,4-diazoniabicyclo[2.2.2]octanium dichloride, MPTC) as catalyst under sonication (40 kHz, 300 W). As shown in Table 1 (Entry 1), there was an increase in the reaction rate or conversion from 0 to 300 rpm. The rate of the reaction was almost same for the stirring speed from 300 to 500 rpm. This indicates the absence of external mass-transfer beyond 300 rpm<sup>9</sup>. This result indicates that the reaction is carried out in a solid-liquid condition. All the further reactions are carried out 400 rpm while assessing the effect of other variables on the reaction rate. The  $k_{app}$  values indicate that the mechanical effects brought up by the use of low frequency ultrasounds are responsible of the enhancement of the kinetics by harsh mixing, enhancement of mass transfer<sup>22</sup>. In SL-PTC systems, the implosion of the cavitation bubbles and the concurrent phenomenon of micro streaming of solvent jets onto the solid surface can also lead to fragmentation of the solid particles, increasing the area available for mass transfer. Sonication also sweeps away reactive intermediates produce from the solid surface, renewing the surface for reaction<sup>24</sup>. The potassium salt of isopropyl alcohol is dissolved in toluene in the presence of MPTC and the intrinsic reaction takes place at the bulk organic phase.

The reactions are carried out in three different conditions such that,

- (1) Stirring without sonication (400 rpm only):  $k_{app} = 7.05 \times 10^{-3}, \text{ min}^{-1}$
- (2) Sonication without stirring (40 kHz, 300 W only):  $k_{app} = 5.31 \times 10^{-3}, \text{ min}^{-1}$
- (3) Combination of both (400 rpm and 40 kHz, 300 W):  $k_{app} = 26.82 \times 10^{-3}, \text{ min}^{-1}$

These results portray the combination of both ultrasound and stirring shows higher kapp value (condition 3) than the other conditions and the kapp value for condition 3 is 3.8 times higher than the condition (1).

**Table 1 (Kinetic variations of the reaction of isopropanol with 1-chloro-4-nitrobenzene)**

Entry	Variations	$k_{app} \times 10^3, \text{ min}^{-1}$ (40 kHz, 300 W)
1.	Stirring speed (rpm)	
	0	5.31
	100	12.32
	200	19.67
	300	26.82
	400	26.93
	500	30.01
2.	MPTC (mol%)	
	1	16.21
	2	21.07
	3	26.82
3.	1-chloro-4-nitrobenzene (g)	
	0.6	16.98
	0.8	21.56
	1.0	26.82
	1.2	30.48
	1.4	33.79
4.	phase-transfer catalysts (3mol%)	
	MPTC	26.82
	TOAB	22.43
	THAB	19.89
	TBAB	18.76
	TEAB	15.45
5.	KOH (g) and H <sub>2</sub> O (mL)	
	5 in (2mL H <sub>2</sub> O)	18.45
	10 in (2mL H <sub>2</sub> O)	26.82
	15 in (2mL H <sub>2</sub> O)	28.34
	10g in (3mL H <sub>2</sub> O)	25.61
	10g in (4 mL H <sub>2</sub> O)	23.39
	10g in (6 mL H <sub>2</sub> O)	20.21
	10g in (8 mL H <sub>2</sub> O)	17.11

**Reaction conditions:** 10 g of KOH, in 2 mL H<sub>2</sub>O, 0.2 g of biphenyl (internal standard), 10 mL of isopropyl alcohol, 1 g of 1-chloro-4-nitrobenzene, 30 mL of toluene, 400 rpm, 50°C; ultrasound condition (40 kHz, 300 W).

## 8.2. Effect of MPTC concentrations

The kinetic experiments were conducted by the series of MPTC concentrations as 1 mol% to 3 mol% by keeping other experimental parameters are kept constant under the sonication (40 kHz, 300W). From the Table 1 (Entry 2), we can see that the rate of conversion is increased with increasing in the amount of MPTC along with ultrasound irradiation (40 kHz, 300W). The conversion is increased with increase in the MPTC concentration linearly from 1 mol % to 3 mol %. The increase in the  $k_{app}$  value is attributed to the synergic effect of ultrasound might be enlarged<sup>8</sup>. The small amount of water (trace) can efficiently promote the solubilization of the solid reactant and thus enhance the formation of catalytic intermediate. We believe that ultrasound can also perform a function similar to that of traces of water in an SLPTC system by weakening the crystal lattice structure of the solid reagent, and thereby enabling the PT catalyst to easily ion exchange at the solid surface. Therefore all the subsequent experiments were done at 3 mol % of catalyst concentration.<sup>25</sup>

## 8.3. Effect of the concentration of p-chloronitrobenzene

To investigate the influence of 1-chloro-4-nitrobenzene (CNB) on the kinetics of synthesis of 1-(isopropoxy)-4-nitrobenzene under ultrasonic irradiation condition (40 kHz, 300 W), the amount of 1-chloro-4-nitrobenzene was varied from 0.6 g to 1.4 g. The results are shown in Table1 (Entry 3). The data clearly indicates that the  $k_{app}$  value increases with increasing the amount of CNB. When the 1-chloro-4-nitrobenzene concentrations increased, the probability of finding the substrate with active-site of the catalyst is increased and resulted in the higher rate of the reaction. The ultrasound enhanced the rate of the reaction,<sup>8</sup> it may be due to reduces the surface area between the solid and organic phases, and hence more reactants collide to each other simultaneously we get higher  $k_{app}$  value.

## 8.4. Effect of temperature

To find out the effect of temperature on the reaction of isopropyl alcohol with 1-chloro-4-nitrobenzene was studied under otherwise similar reaction conditions. The temperature was varied from 40°C to 70°C. The kinetic profile of the reaction is obtained by plotting  $-\ln(1-X)$  versus time. It is obvious that the reactivity is increased with an increase in the temperature along with ultrasonic effect.<sup>7,8</sup> The reason behind is,

- The number of reactant molecules which possess higher activated energy at a higher temperature and thus the ultrasonic wave easily passes through the reactor.
- The collision of the reactants at higher temperature is also increased.

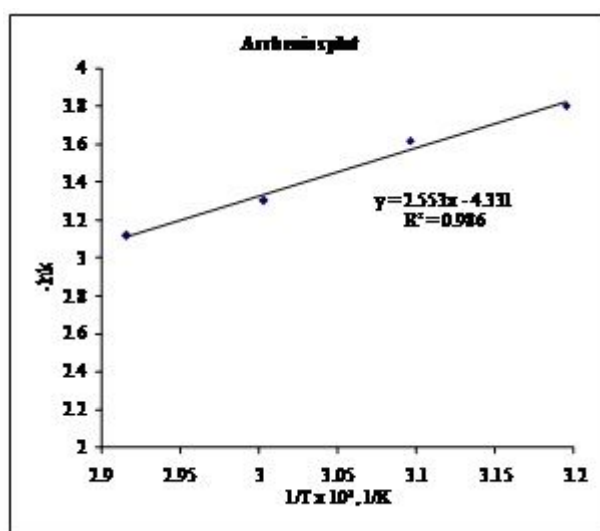


Figure 1 (Arrhenius plot)

Hence, the apparent rate constant is increased at higher temperature. Arrhenius plots were made in Figure 1 of  $-\ln k_{app}$  against  $1/T$  to get activation energy of 48.9 kJ.mol<sup>-1</sup>. This higher activation energy demonstrates that, this reaction was kinetically controlled and the mass-transfer resistance between phases was unimportant. In addition ultrasound is used to overcome the mass-transfer resistant and avoid the use of higher

temperature for the reaction system. It is evident from higher activation energy and higher stirring speed that the present reaction system follows the interfacial mechanism.<sup>26,27</sup>

Arrhenius plot; 10 g of KOH in 2 mL H<sub>2</sub>O, 0.2 g of biphenyl (internal standard), 10 mL of isopropyl alcohol, 1g of 1-chloro-4-nitrobenzene, 3 mol% MPTC, 30 mL of toluene, 50°C, 400 rpm, ultrasound condition (40 kHz, 300W).

### 8.5. Effect of phase-transfer catalysts

In this experiment, besides MPTC, four different phase-transfer catalysts are employed to evaluate their influence in the reaction of isopropyl alcohol and 1-chloro-4-nitrobenzene in the presence of sonication keeping similar reaction conditions. The employed MPTC is 1,4-dibenzyl-1,4-diazoniabicyclo[2.2.2]octanium dichloride and the PTCs are TOAB, THAB, TBAB and TEAB. The pseudo-first order rate constant are evaluated for all the catalyst from the plot of  $-\ln(1 - X)$  versus time. Table 1 (Entry 4) depicts the apparent rate constant for these catalyst, in which MPTC's shows higher activity. The order of catalyst efficient activities are MPTC > TOAB > THAB > TBAB > TEAB. These results indicate the lipophilic character of the catalysts and MPTC has the ability to coordinate with more number of anions and transfer the catalytic intermediate to the reactions medium. The results also indicate an additional increase of  $k_{app}$  value when the reaction was carried out under MPTC and ultrasound irradiation condition 40 kHz, 300 W. It may be due to the change in the size, surface area and morphology of phase-transfer catalysts due to the positive effect of ultrasound.

### 8.6. Effect of various potassium hydroxide concentration and volume of water

Kinetic experiments were carried out, by employing 5g, 10g and 15g of KOH (in 2 mL water) under otherwise similar reaction conditions. The  $k_{app}$  values tremendously increased with increasing in the basicity of OH<sup>-</sup> ion. To check the  $k_{app}$  value for the volume of water added to the reaction mixture by keeping 10 g of KOH as constant. Potassium hydroxide itself dissolved in the alcohol and produces the potassium salt of anion in the absence of water. The volume of water is varied as 2, 3, 4, 6, 8 mL by keeping the other similar reaction conditions. Addition of trace amount of water (up to 2 mL) increases the reaction rate. But after the 2 mL, the reaction rate decreases gradually as the volume of water increases and then the reaction system is converted to liquid-liquid reaction when the volume of water is 8 mL (Table 1-Entry 5).

### 8.7. Effect of different alcohol

Potassium salts of alcohols were prepared in situ by reacting different alcohols and the well powdered potassium hydroxide. These salts were reacted under identical reaction conditions with 1-chloro-4-nitrobenzene (CNB) using MPTC as the catalyst under sonication (40 kHz, 300W). The 4-nitrophenyl alkyl ethers were the only products of these reactions evidenced by thin layer chromatography (TLC) and GC measurement. The conversions after 60 min were listed in the Table 2. The conversion is gradually decreased by chain length is increased. Low reactivity of isopropanol can be accounted by steric hindrance caused by isopropyl group in the ether linkage (Table 2).

### 8.8. Discussion for the Path II reactions

The alternative method (Path-II) is tried to get the same product of path-I (Scheme 2). In this process, the 4-nitrophenol (4 g) and potassium carbonate (10 g) in 2 mL water taken in the 250 mL RB flask and known quantities of toluene (30 mL, solvent), alkyl halides (6 mmol), 0.2 g biphenyl (IS-internal standard), 3 mol % of the newly synthesized MPTC were introduced to the reactor to start the reaction. The reaction mixture was stirred at 400 rpm. The samples are taken at chosen time intervals from the organic phase and analyzed by GC. The conversion of the reactant is placed in the Table 2.

**Table 2 (Synthesis of 4-nitrophenyl alkyl ethers from two path ways)**

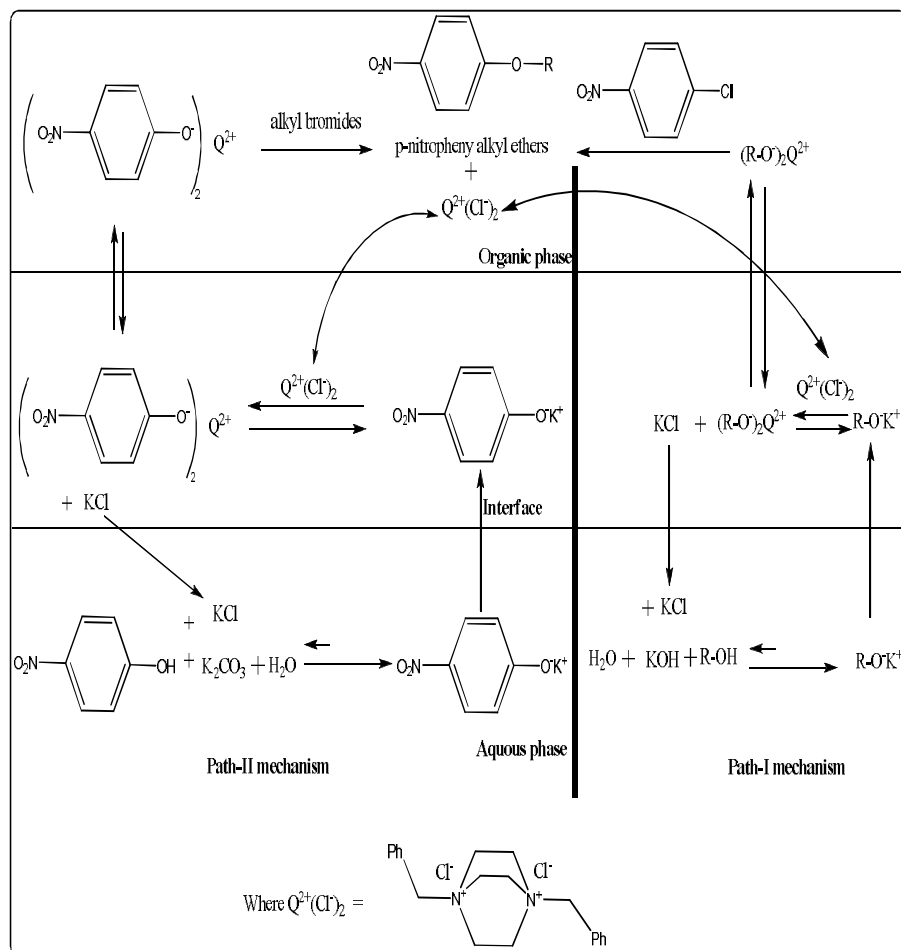
Entry	Products	% Conversion	
		Path-I	Path-II
1.		94	100
2.		80	90
3.		76	93
4.		74	90
5.		72	87
6.		70	85

**Path I:** 10 g of KOH, in 2 mL H<sub>2</sub>O, 0.2 g of biphenyl (internal standard), 10 mL of different alcohols, 1 g of 1-chloro-4-nitrobenzene, 30 mL of toluene, 400 rpm, 50<sup>0</sup>C; ultrasound condition (40 kHz, 300W).

**Path II:** 10 g of K<sub>2</sub>CO<sub>3</sub>, in 2 mL H<sub>2</sub>O, 0.2 g of biphenyl (internal standard), 4 g of 4-nitrophenol, 6 mmol of alkyl bromides, 30 mL of toluene, 400 rpm, 50<sup>0</sup>C; ultrasound condition (40 kHz, 300W).

### 8.9. Mechanism

The solid-liquid reaction mechanisms are classified into two categories. First one is the non-soluble system (heterogeneous solubilization) introduced by Doraisamy and Naik<sup>28</sup> and other is soluble system (homogeneous solubilization) introduced by Yadav and Sharma<sup>29</sup>, which depend on the solubility of the inorganic salt of anion in the organic solvent. In this work, potassium salt of isopropyl alcohol is sparingly soluble in organic solvent (toluene). First, potassium salt of isopropyl alcohol dissolved in the organic solvent with the addition of quaternary ammonium salt. The inorganic salt KX precipitated as a solid form in the organic solution and then it is transported to the aqueous or solid phase. In a similar way, Vander and Hartner<sup>30</sup> and Yoel and Zahalka<sup>31</sup> proved that quaternary ammonium salt can be used to dissolve the solid reactant. The active intermediate C<sub>3</sub>H<sub>7</sub>-O<sup>-</sup>Q<sup>+</sup> (org) then react with 1-chloro-4-nitrobenzene (CNB) to produce the desired product (Scheme 3) and the catalyst is regenerated and the above said cyclic process take place continuously up to the disappearance of 1-chloro-4-nitrobenzene in the bulk organic phase.

**Scheme 3 (Mechanism for etherification)**

## 9. Conclusion

From the present kinetic study, the following conclusions are revealed,

1. The formation of 4-nitrophenyl alkyl ethers from alcohols and 1-chloro-4-nitrobenzene (CNB) under ultrasonic-MPTC condition. The same products were obtained from 4-nitrophenol and alkyl halides.
2. The apparent reaction rates were observed to obey the pseudo-first order kinetics.
3. Sonication resulted in shorter reaction time, selectivity, high yield, etc.
4. The apparent rate constants were increased with increases in the concentration of MPTC, concentration of KOH, stirring speed and temperature.
5. However it decreases with increase in the volume of water.
6. Energy of activation was calculated from the Arrhenius plot and interfacial mechanism was proposed for the present reaction system.
7. Combination of ultrasound and MPTC resulted in better efficacy as compared to the individual operations.

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