Ultrasound assisted dichlorocarbene addition to 1,3-bis(allyloxy)-5-methylbenzene under biphasic condition: A kinetic study

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Abstract
A new multi-site phase-transfer catalyst (MPTC), viz., N,N’-dioctyl-4,4’-bipyridium dibromide containing bi-site was prepared and was also proved by FT-IR, \textsuperscript{1}H NMR, \textsuperscript{13}C NMR, mass and elemental analysis. The enhancement of C-N\textsuperscript{+} peak intensity at 1179 cm\textsuperscript{-1} was noticed in FT-IR, and the agreement of m/z values, viz., 542.43 bi-site with their theoretical values and the percentage of C, H, N elements noticed in elemental analysis has strongly supported the presence of tri-site MPTC catalysts. Further, the presence of number of active-sites in the catalyst was again confirmed by determining their pseudo-first order rate constant for dichlorocarbene addition to 1,3-bis(allyloxy)-5-methylbenzene in the presence of ultrasonic irradiation/mechanical stirring. The comparative study reveals that the k\textsubscript{app} determined by the combination of ultrasound and mechanical stirring has shown more activity than by their individual effect. Further, the detailed kinetic study performed with superior di-site MPTC reveals that the k\textsubscript{app} are dependent on the stirring speed, [substrate], [catalyst], [NaOH] and temperature. Finally, based on the kinetic results, thermodynamic parameters are evaluated.

Keywords: Ultrasound irradiation; dichlorocarbene; phase-transfer catalysis; kinetic study.

Introduction
Phase-transfer catalysis (PTC) is an important method that allows many organic reactions to run heterogeneously. [1-4]. PTC has found numerous applications in all essential fields of organic syntheses, industrial chemistry, biotechnology, and material sciences. It can be encountered in the manufacture of advanced pharmaceuticals, fragrance, crop protection chemicals, highly advanced engineering plastics, material for semiconductors, and electro-optical and data storage devices [5,6].

Even though, various soluble single-site PTC have been extensively used for a number of organic reactions, but again because of its inseparability, its usage is often limited. In order to
recover the catalyst for reuse, the soluble single-site PTC has been immobilized onto the polymer matrices and thus their insoluble heterogeneous single-site phase-transfer catalyst is derived. However, because of its lower activity and diffusion limitation the applicability of insoluble heterogeneous single-site phase-transfer catalyst has always received poor attention among the stakeholders. Subsequently, with a view to improve further catalytic efficiency, soluble form of multi-site phase transfer catalyst has emerged and been used for various organic reactions especially in biphasic medium.

Idoux et al. [7] were the first to report the soluble and insoluble polymer supported phosphonium multi-site PTCs having three active sites. The effectiveness of the catalytic activities of these ‘multi-site’ PTCs towards simple SN2 reactions and some weak nucleophile, electrophile reactions were also reported. The most significant merit for MPTCs is that it has an ability to transfer more number of anionic species (M\(^+\)Y\(^-\)) from aqueous phase to organic phase. In contrast, the single-site quaternary onium phase transfer catalyst can transfer only one molecule of anionic species, i.e., M\(^+\)Y\(^-\) from aqueous phase per cycle. Especially, nowadays much emphasis has been given to economy of scale and efficiency of onium salts particularly for the industrial scale preparation of organic compounds. Balakrishnan et al. [8–10] have developed soluble multi-site phase transfer catalyst containing two and three active sites to catalyze the various organic reactions. Wang et al. [11,12] also reported a kinetic study of dichlorocyclopropanation of 4-vinlycyclohexene and etherification of 4,4-bis(chloromethyl)-1,1-biphenyl and 1-butanol catalyzed by using soluble MPTC containing two active sites and showed that MPTC exhibits more reactivity than single-site PTC. In our laboratory too, multi-site phase transfer catalysts are reported for polymerization under heterogeneous condition [13]. Particularly, if the dichlorocarbene reaction is performed with “multi-site PTCs” then the rate of the reaction rises, because, the MPTCs generate more dichlorocarbene and thus lead to effective addition to the olefins. In 1969, Makosza and Wawrzyniewicz [14] were the first to report the dichlorocarbene addition reaction under biphasic conditions, high yield of dichlorocyclopropane product was obtained by using 50% NaOH and chloroform in excess. Subsequently, various reports have appeared for the dichlorocarbene addition in different olefins using PTCs [11, 15-17].

In recent years, the application of ultrasound irradiation in organic synthesis has been broadly extended. It can increase the rate of reaction, yield and the selectivity of desired product under very milder condition [18-21]. Hence, ultrasound technique has been considered as a convenient and environmentally benign technique [18, 22-27]. Several studies have been already reported in which it is observed that the combination of PTC with ultrasound is proved to be an effective technique for organic transformations compared to what was in silent condition [28-33]. The Cannizarro reaction catalyzed by a PTC under ultrasonic condition showed that an ultrasonic wave of 20 kHz dramatically accelerated the rate of the reaction [34]. Wang et al. investigated the liquid–liquid multi-site phase-transfer catalyzed epoxidation and dichlorocyclopropanation of 1,7-octadiene and ethoxylation of \( p \)-chloronitrobenzene assisted by ultrasound energy, the reaction rates
were greatly enhanced in all the reactions [35-37]. In the past efforts, the application of ultrasound in liquid−
liquid phase transfer catalysis was rarely studied. However, to the best of our knowledge, there is no report available on the kinetics of dichlorocarbene addition to 1,3-
bis(allyloxy)-5-methylbenzene using soluble single and dual-site PTC along with ultrasonic irradiation. Hence, in this study, we have aimed at preparing a new multi-site phase transfer catalyst, viz., moreover, N,N'-dioctyl-4,4'-bipyridinium dibromide (MPTC) was synthesized through simplified procedures with inexpensive starting materials. Further, the catalytic activity of newly prepared MPTC and commercial single-site PTC were studied with dichlorocarbene addition to 1,3-bis(allyloxy)-5-methylbenzene under pseudo-first order rate condition in biphasic medium combined with ultrasonic irradiation (denoted as “>>>>”) in a batch reactor.

**Experimental**

**Chemicals**

The reagents were used as received (SRL): Orcinol, chloroform, diethyl ether, sodium hydroxide, chlorobenzene, potassium hydroxide, allyl bromide, tetrabutylammonium chloride (TBAC), tetrabutylammonium bromide (TBAB), tetrabutylammonium iodide (TBAI), and tetrabutylammonium hydrogensulphate (TBAHS).

**Instrumentation**

The FT-IR spectra were recorded on a Bruker-Tensor 27 FT-IR spectrophotometer. The $^1$H NMR and $^{13}$C NMR spectra were recorded using Bruker 400 MHz spectrometer. The mass spectra were recorded on a JEOL GC mate mass spectrometer. Elemental analysis was performed on a Perkin-Elmer 240B elemental analyzer. The ultrasonic generator (model RZ-08895-22) was a thermostatic water bath equipped with dual frequencies 28 kHz (300W) and 40 kHz (300W). The kinetics of the dichlorocarbene addition to 1,3-bis(allyloxy)-5-methylbenzene was studied by quantitative analysis of sample with a gas chromatography (Varian-3700 interfaced with a chromatograph I/F module) system that included a flame ionization detector. The column used for the product analysis was a 5% SE-30, chrome WHP 80/100, 3 m × 1/8 in., stainless steel tube.

**Synthesis of dual-site phase-transfer catalyst (MPTC)**

The dual-site phase-transfer catalyst (MPTC) was synthesized by reacting 1.56 g (10 mmol) of 4,4'-bipyridien with 20 mL of n-octylbromide 60 mL of acetonitrile in a 250 three necked round bottomed Pyrex flask. At 500 rpm and 70 °C for 24 h in the nitrogen atmosphere. After removing acetonitrile from the reaction mixture, methyl tert-butyl ether (MTBE, 25 mL) was added to precipitate white solids, which were then separated by centrifugation. The re-dissolution by acetone and re-precipitation by MTBE were repeated at least three times, and the final solids were separated and dried at 60 °C for 1 h to get N,N’-dioctyl-4,4’-bipyridium dibromide (dual-site MPTC). The catalyst was identified with $^1$H-NMR, $^{13}$C-NMR and elemental analysis. $^1$H NMR (400 MHz, DMSO); δ 0.87-0.89 (t,6H-CH$_2$-CH$_3$), 1.29-1.39 (m,20H-CH$_2$-CH$_3$), 2.08-2.14 (q,4H-N$^+$-CH$_2$-CH$_3$), 4.69-4.75 (m,4H-N$^+$-CH$_2$), 60.4 (N$^+$-pyCH $^+$), 8.47-8.59 (dd,4H, pyCH $^+$), 9.02-9.15 dd, H, N$^+$-pyCH $^+$; $^{13}$C NMR (100 MHz CDCl$_3$); δ 11.9 CH$_3$, 20.5, 23.7, 26.6, 26.7, 29.1, 29.5. (CH$_2$), 60.4 (N$^+$-CH$_2$),
Preparation of 1,3-bis(allyloxy)-5-methylbenzene

To a mixture of KOH (15 g, 0.26 mol) in water (15 mL) and \(N,N'\)-dioctyl-4,4'-bipyridinium dibromide (MPTC) (0.5 g, 0.92 mmol), orcinol (2.5 g, 0.022 mol) was added under overhead stirring to generate the 5-methyl-1,3-diphenoxide anion. Then allyl bromide (6.34 g, 0.052 mol) in chlorobenzene (40 mL) was added slowly. The reaction mixture was heated at 45°C for 6 hours with stirring (500 rpm). The crude product was isolated by simple extraction with three times diethyl ether (5 mL). The organic layer was collected and the solvent was evaporated under reduced pressure. The crude product was chromatographic (SiO\(_2\)) employing hexane: ethyl acetate (9:1) as eluent to obtain pure compound viz., 1,3-bis(allyloxy)-5-methylbenzene. The product was confirmed by \(^1\)H NMR and \(^{13}\)C NMR spectra of the product. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 2.32 (s,3H, CH\(_3\)), 4.45-4.47 (d,4H, O-CH\(_2\)), 5.22-5.41 (2dd, 4H, C=C-CH\(_2\)), 5.95-6.08 (m,2H, C=C-CH), 6.48-7.16 (m,4H, Ar-CH). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 68.8 (O-CH\(_2\)), 117.6 (HC=CH\(_2\)), 133.5 (H\(_2\)=C=CH), 114.9, 120.9, 129.9, 158.7 (Ar-CH). MS (EI, 70 Ev, %): m/z 204.

Kinetics of dichlorocarbene addition to 1,3-bis(allyloxy)-5-methylbenzene

According to our experimental condition the mono-substituted product i.e., 1-(2,2-dichlorocyclopropyl)methoxy)-3-(allyloxy)-5-methylbenzene (A) (Scheme 3) was not found. Only di-substituted product viz., 1,3-bis((2,2-dichlorocyclopropyl)methoxy)-5-methylbenzene (B) (Scheme 3) was produced from the reaction solution containing 1,3-bis-(allyloxy)-5-methylbenzene. The kinetics of the reaction was performed in an ordinary 150 mL three-necked round bottom flask. The reaction mixture was heated at 50°C for 6 hours with stirring (500 rpm). The crude product was isolated by simple extraction with three times diethyl ether (5 mL). The organic layer was collected and the solvent was evaporated under reduced pressure. The crude product was chromatographic (SiO\(_2\)) employing hexane: ethyl acetate (9:1) as eluent to obtain pure compound viz., 1,3-bis(allyloxy)-5-methylbenzene. The product was confirmed by \(^1\)H NMR and \(^{13}\)C NMR spectra of the product. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 2.32 (s,3H, CH\(_3\)), 4.45-4.47 (d,4H, O-CH\(_2\)), 5.22-5.41 (2dd, 4H, C=C-CH\(_2\)), 5.95-6.08 (m,2H, C=C-CH), 6.48-7.16 (m,4H, Ar-CH). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 68.8 (O-CH\(_2\)), 117.6 (HC=CH\(_2\)), 133.5 (H\(_2\)=C=CH), 114.9, 120.9, 129.9, 158.7 (Ar-CH). MS (EI, 70 Ev, %): m/z 204.
flask fitted with flat-bladed stirring paddle and a reflux condenser. The dichlorocarbene addition of 1,3-bis(allyloxy)-5-methylbenzene reaction was carried out by reverse addition method, i.e., by delayed addition of 1,3-bis(allyloxy)-5-methylbenzene. To the reaction flask, 30 mL of (30 wt %) aqueous NaOH, 0.72 mmol of respective phase-transfer catalyst and 20 mL chloroform (solvent) were added and stirred at 100 rpm for 5 min at 40°C to stabilize the catalyst. 1,3-bis(allyloxy)-5-methylbenzene (1.5g, 7.35 mmol) in 10 mL chloroform preheated to 40°C was added to the reaction mixture at zero time. The reaction mixture was stirred at 200 rpm and the ultrasonic energy (28 kHz and 300 W) was simultaneously passed through the reactor. Samples were collected from the organic layer of the mixture at regular intervals of time and each run consists of the six samples. The kinetics of the reaction was followed by estimating the amount of 1,3-bis(allyloxy)-5-methylbenzene disappeared using gas chromatograph. An aliquot of reaction mixture (1µl) was injected into the column and the product was analyzed. The retention time for each compound was noted as, chloroform (0.71 min) 1,3-bis(allyloxy)-5-methylbenzene (1.14 min), and 1,3-bis((2,2-dichlorocyclopropyl)methoxy)-5-methylbenzene (4.50 min). The pseudo-first order rate constants were calculated from the plots of $-\ln(1-X)$ versus time. The kinetic experiments were carried out in duplicate to confirm reproducibility of the results.

**Scheme 3.** Preparation of 1,3-bis((2,2-dichlorocyclopropyl)methoxy)-5-methylbenzene

**Results and discussion**

Nowadays, phase transfer catalysis is a vital and very fascinating technique to conduct the reaction between immiscible reactants available in the heterogeneous system. In order to perform this immiscible substrate reaction more effectively, many
researchers have devoted their attention to develop multi-site phase-transfer catalyst (more than one site) to replace the low active single-site PTC. Particularly, dichlorocarbene addition to olefins using multi-site phase-transfer catalyst (MPTCs) aided by ultrasonic energy is an active area for current study. To strengthen further, a new dual-site phase-transfer catalyst viz., \(N,N'\)-dioctyl-4,4'-bipyridinium dibromide (MPTC) was prepared. The catalytic activity of MPTC was employed for dichlorocarbene addition to 1,3-bis(allyloxy)-5-methylbenzene along with ultrasonic irradiation (28 kHz, 300 W). The pseudo-first order rate constant was determined by measuring the disappearance of 1,3-bis(allyloxy)-5-methylbenzene under regular intervals using gas chromatography.

Generally, the effect of ultrasonic energy for the promotion of dichlorocarbene addition to 1,3-bis(allyloxy)-5-methylbenzene was caused by the production of intense local conditions due to cavitations bubble dynamics, i.e., the nucleation, formation, disappearance and coalescence of vapors or gas bubbles in the ultrasonic field [38-42]. However, in phase transfer catalyst reactions, rate enhancements are typically due to mechanical effects, mainly through an enhancement in mass transfer. In liquid–liquid bi-phase system, the presence of ultrasonic wave energy used to disrupt the interface by cavitations collapse near the liquid–liquid interface and impels jets of one liquid into other, forms fine emulsions and leads to a dramatic enhancement in the interfacial contact area through which transfer of species can take place [43]. Therefore, the combination of PTC and ultrasound energy has proved to be a best and environmentally benign catalytic method to conduct the organic addition reaction [38-46]. In view of the impact of ultrasonic energy, it is decided to conduct detailed kinetic study for dichlorocarbene addition to 1,3-bis(allyloxy)-5-methylbenzene using the superior new dual-site phase-transfer catalyst, viz., \(N,N'\)-dioctyl-4,4'-bipyridinium dibromide (MPTC) in association with ultrasonic wave energy and by varying the experimental parameters such as [substrate], [PTC], [NaOH], and temperature.

**Ultrasound Energy**

In the present work, we investigate the effect of ultrasound energy on the dichlorocyclopropanation of 1,3-bis(allyloxy)-5-methylbenzene. Ultrasound generates extremely fine emulsions which provide enormous interfacial contact areas between immiscible liquid and thus is the potential for greater reaction in the phase. This can be particularly beneficial in phase-transfer catalysis [44-48]. The combination of ultrasound irradiation with phase-transfer catalysis could give synergy effect in catalysis and the reaction rate could be greatly promoted [18, 35, 36, 46, 49, and 50].

The ultrasound-assisted dual-site phase-transfer catalyst, viz., \(N,N'\)-dioctyl-4,4'-bipyridinium dibromide (MPTC) was carried out in a thermostatically batch reactor equipped with ultrasonic generator 28 kHz with output power of 300W. The reaction rate was also compared with 0 kHz and 40 kHz (300W). The effect of the ultrasonic frequency on the rate \(k_{\text{app}}\) was represented in Table 1. In our study at 50 min, in the presence of ultrasonic irradiation, 200 rpm the \(k_{\text{app}}\) of the reaction increased to almost 3.86 times and 2.04 times faster for 28 kHz (300W) & 40 kHz (300W) than without ultrasonic irradiation i.e., under silent...
condition. From these observations, it was inferred that the ultrasonic assisted multi-site phase-transfer catalyst significantly increased the $k_{app}$. The product yield decreased with increasing ultrasonic frequency (Table 1) in the order of $k_{app}$ being 28 kHz > 40 kHz > 0 kHz. The reaction rate at 40 °C with ultrasound (28 kHz) was 3.86 larger than that at silent condition, showing the reaction rate effectively enhanced by ultrasound (Table 1) is the variation of the tested ultrasonic frequencies, showing the fastest intrinsic reaction rate at 28 kHz resulted in the highest consumption rate of $Q \; (CCl_3)_2$ (Scheme 4).

**Table 1. Effect of ultrasonic energy**

<table>
<thead>
<tr>
<th></th>
<th>0 kHz $k_{app} \times 10^2$ (min$^{-1}$)</th>
<th>28 kHz $k_{app} \times 10^2$ (min$^{-1}$)</th>
<th>40 kHz $k_{app} \times 10^2$ (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.99</td>
<td>22.89</td>
<td>10.18</td>
<td></td>
</tr>
</tbody>
</table>

Effect of ultrasonic energy on the apparent rate constants: 7.35 mmol of 1,3-bis(allyloxy)-5-methylbenzene, 30 mL of chloroform, 0.92 mmol of MPTC, 30 mL of NaOH solution (30 wt.%), 40 °C.

Scheme 4. Reaction mechanism
Effect of the agitation speed

The effect of agitation speed on the rate of dichlorocarbene addition to 1,3-bis(allyloxy)-5-methylbenzene using a dual-site phase-transfer catalyst viz., N,N′-dioctyl-4,4′-bipyridinium dibromide (multi-site phase-transfer catalyst, MPTC), the reaction was studied by varying the agitation speed in the range of 100–1000 rpm along with ultrasonic irradiation 28 kHz (300W). The other parameters such as [substrate], [MPTC], [NaOH] and temperature were kept constant. The pseudo first order rate constants were evaluated from the plots of –ln(1-X) versus time (Figure 1).

![Figure 1. Effect of Agitation speed](image)

From the observed $k_{app}$, it is understood that the rate of the reaction increases on increasing the agitation speed, i.e., the rate constant was gradually increased from 100 to 200 rpm and then the rate constant of the reaction was not improved on increasing the stirring speed above 200 rpm. Similar trend of observation is already reported in effect of varying the stirring speed [11,55] and it was suggested that the reaction has followed interfacial mechanism. In the present study also, $k_{app}$ is independent of the stirring speed at above 200 rpm, and this trend indicates that the reaction has proceeded through interfacial mechanism. In general, phase transfer catalysis reaction stirring speed is a vital role along with ultrasound energy. Hence, the $k_{app}$ value higher than the conventional method (Figure 1).

Effect of substrate concentration

The effect of varying the concentration of 1,3-bis(allyloxy)-5-methylbenzene on the rate of dichlorocarbene addition was studied in the range of 4.90-14.70 mmol while keeping the other reagents constant under the ultrasonic irradiation condition. The pseudo-first order rate constants were evaluated (Table 2). The observed rate constants were increased on increasing the amount of substrate. This observation may be due to the presence of more number of active sites in the multi-site phase-transfer catalyst (MPTC) and higher concentration of substrate which had cooperatively influenced the reaction and thus enhanced more numbers of contacts between catalyst and substrate and hence reflected in enhanced $k_{app}$.

Balakrishnan et al. reported similar results in the study of C-alkylation of phenyl acetone [52] and phenylacetonitrile [8] with n-bromobutane using PTC. Recently, Murugan et al. [53] have also reported the same dependency of rate constants for the dichlorocarbene addition to citral and α-pinene using multi-site phase-transfer catalyst.
Table 2. Effect of substrate

<table>
<thead>
<tr>
<th>1,3-bis(allyloxy)-5-methylbenzene (mmol)</th>
<th>4.90</th>
<th>7.35</th>
<th>9.80</th>
<th>12.25</th>
<th>14.70</th>
</tr>
</thead>
<tbody>
<tr>
<td>With ultrasonic (28 kHz, 300 W).</td>
<td>(k_{\text{app}} \times 10^2) (min(^{-1}))</td>
<td>12.89</td>
<td>22.98</td>
<td>28.22</td>
<td>31.42</td>
</tr>
<tr>
<td>Without ultrasonic (0 kHz).</td>
<td>(k_{\text{app}} \times 10^2) (min(^{-1}))</td>
<td>3.08</td>
<td>5.19</td>
<td>7.66</td>
<td>8.06</td>
</tr>
</tbody>
</table>

Effect of 1,3-bis(allyloxy)-5-methylbenzene on the apparent rate constants: 30 mL of chloroform, 0.92 mmol of MPTC, 30 mL of NaOH solution (30 wt.%), 40°C, (28 kHz, 300 W).

**Effect of MPTC concentration**

The effect of concentration of dual-site phase-transfer catalyst, viz., \(N,N'\)-dioctyl-4,4'-bipyridinium dibromide (MPTC) on the rate of the dichlorocarbene addition to 1,3-bis(allyloxy)-5-methylbenzene was studied in the range of 0.39-1.04 mmol while keeping the other experimental parameters constant under the ultrasonic irradiation (28 kHz, 300 W) condition. The pseudo-first order rate constants were evaluated from the plot of \(-\ln(1-X)\) versus time. From the observed results, the rate constants are linearly dependent on the concentration of catalyst (Figure 2). The increased rate constants are attributed to increase in number of catalytic active site (N\(^+\)) which in turn can enhance more number of effective collisions between \(\text{Na}^+\text{CCl}_3\) and MPTC in the interface. In other words, at higher concentration of MPTC, the generation of dichlorocarbene (:CCl\(_2\)) have been increased which in turn leads to increase in the formation of complex, \(Q(\text{CCl}_3)\text{PTC}\) in the organic phase. Further, not only higher rate of reactions were obtained due to the presence of more amount of phase-transfer catalysts but also intensification of the rate had occurred [56] and also there was a total suppression of side reactions leading to 100% selectivity of the product. The control experiments (without stirring and 0 kHz) were also carried out for dichlorocarbene addition to 1,3-bis(allyloxy)-5-methylbenzene. The linear dependence of the reaction rate constants on [MPTC] shows that the reaction is believed to proceed through the interfacial mechanism. The bilogarithmic plot of the reaction rate constant versus the concentration of the catalyst gave a straight line with a slope of 1.18. Similar report was observed by Starks [54] in the study of dichlorocarbene addition to cyclohexene using tridecylmethylammonium chloride as catalyst. Halpern et al. [55] have studied the dehydrobromination of phenethyl bromide using tetraoctylammonium bromide as a catalyst, zero order kinetics with respect to the catalyst amount was observed. The kapp value at 400C with ultrasound (28 kHz, 300W) was larger than that at silent condition, indicating that the reaction rate was effectively enhanced by ultrasonic irradiation.
Comparison of apparent rate constants with different phase-transfer catalysts
Quaternary ammonium salts are generally used as phase-transfer catalyst to promote reaction rate for immiscible reactions. In addition to ultrasound irradiation condition (28 kHz, 300W) five different phase-transfer catalysts along with a new synthesized dual-site phase-transfer catalyst (MPTC) were used for dichlorocarbene addition to 1,3-bis(allyloxy)-5-methylbenzene. The four other single-site quaternary ammonium salts, such as tetrabutylammonium chloride (TBAC), tetrabutylammonium bromide (TBAB), tetrabutylammonium iodide (TBAI), and tetrabutylammonium hydrogensulphate (TBAHS) were investigated in order to test their relativities. The corresponding $k_{app}$ values are depicted in Table 3. The order of the reactivates in choosing the tetrabutylammonium cation group in this work is TBAHS > TBAC> TBAB> TBAI. Choosing a small size of the anionic ion in the halide groups of PTCs is favorable for a high reaction rate [56]. This phenomenon is more consistent with the interfacial reaction mechanism rather than the extraction reaction mechanism [46]. $N,N'$-dioctyl-4,4'-bipyridinium dibromide (MPTC) is more reactive then other quaternary salts, due to it is dual active site and lipophilic nature may be higher. The activity of the lipophilic cation ($Q^+$ for single site, $Q^{2+}$ for double site) is determined mainly by two factors; its extractability which is depends on organophilicity of the catalyst and the anion pairs ($Q^+$ CCl$_3^-$) for the single-site and $Q^{2+}$ (CCl$_3$)$_2$ for dual-site catalyst). Further, the ultrasonic irradiation can enhance the rate for multi-site phase-transfer catalyst than single-site due to the transference of more ion pare to organic phase where the reaction take place pre cycle. Based
on the above argument the order of the relativities of these quaternary ammonium salts are in order MPTC > TBAHS > TBAC > TBAB > TBAI.

Table 3. Effect of various phase-transfer catalysts

<table>
<thead>
<tr>
<th>PTC</th>
<th>MPTC</th>
<th>TBAHS</th>
<th>TBAC</th>
<th>TBAB</th>
<th>TBAI</th>
</tr>
</thead>
<tbody>
<tr>
<td>With ultrasonic (28 kHz, 300 W). $k_{app} \times 10^2$ (min$^{-1}$)</td>
<td>22.98</td>
<td>15.87</td>
<td>12.54</td>
<td>10.56</td>
<td>09.52</td>
</tr>
<tr>
<td>Without ultrasonic (0 kHz). $k_{app} \times 10^2$ (min$^{-1}$)</td>
<td>5.90</td>
<td>3.91</td>
<td>3.39</td>
<td>2.78</td>
<td>2.69</td>
</tr>
</tbody>
</table>

Effect of the amount of inorganic salt
In this study, sodium bromide was produced as a by-product from the reaction. Therefore, the addition of NaBr naturally affects the equilibrium of each component between the two phases. The results are shown Table 4. The addition of NaBr enhances the reaction as a result of a salting out effect in the aqueous phase and also the formed dichlorocarbene is more favorable to staying in the organic phase. Meanwhile, hydrolysis of dichlorocarbene in the aqueous phase is minimized. For Comparison, the two apparent rate constants obtained from the phase-transfer catalytic reaction [46] in the presence and absence of ultrasonic irradiation are also shown in Table 4. It is obvious that the ultrasonic irritation enhances the reaction.

Table 4. Effect of inorganic salt

<table>
<thead>
<tr>
<th>NaBr (g)</th>
<th>0</th>
<th>0.117</th>
<th>0.585</th>
<th>1.170</th>
<th>1.755</th>
<th>2.925</th>
</tr>
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<tbody>
<tr>
<td>With ultrasonic (28 kHz, 300 W). $k_{app} \times 10^2$ (min$^{-1}$)</td>
<td>22.98</td>
<td>24.60</td>
<td>26.90</td>
<td>29.51</td>
<td>33.68</td>
<td>36.11</td>
</tr>
<tr>
<td>Without ultrasonic (0 kHz). $k_{app} \times 10^2$ (min$^{-1}$)</td>
<td>5.58</td>
<td>6.31</td>
<td>7.08</td>
<td>7.64</td>
<td>8.46</td>
<td>9.06</td>
</tr>
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</table>

Effect of temperature
The effect of varying the temperature on the rate of dichlorocarbene addition to 1,3-bis(allyloxy)-5-methylbenzene was carried out in the temperature range of 303–323 K and keeping the other experimental parameters as constant under the ultrasonic irradiation condition (28 kHz, 300W). The pseudo-first order rate constants were evaluated from the plot of $-\ln(1-X)$ versus time. The observed values indicate that the reaction rate constants were increased on increasing the temperature in association with ultrasonic energy [46, 56]. The energy of activation is calculated from Arrhenius plot (Figure 3), $E_a = 15.76$ kcal mol$^{-1}$. The other thermodynamic parameters such as entropy of activation ($\Delta S^\ddagger$), enthalpy of activation ($\Delta H^\ddagger$) and free energy of activation ($\Delta G^\ddagger$) for dichlorocarbene addition to 1,3-bis(allyloxy)-5-methylbenzene were determined from
Eyring’s equation and the obtained values are 14.7 eu, 15.1 kcal.mol$^{-1}$ and 16.9 kcal mol$^{-1}$ respectively. The activation energy ($E_a$) reported by Chiellini et al. [57] for ethylation of phenylacetonitrile was 20 kcal mol$^{-1}$ and for this an interfacial mechanism was proposed. Reeves and Hilbrich [58] reported that the $E_a$ value for ethylation of pyrrolidin-2-one under PTC condition was 12.4 kcal mol$^{-1}$ and suggested for an interfacial mechanism. Tomi and Ford [59] observed a higher $E_a$ value for the polystyrene bound benzyltriethylammonium ion catalyzed reaction, which was controlled by intrinsic reactivity under triphase reactions. Wang et al. [11] reported that the $E_a$ value for dichlorocyclopropanation of 1,7-octadiene was 13.42 kcal.mol$^{-1}$ and for this also an interfacial mechanism has been proposed. Murugan et al. [53] reported the higher $E_a$ value for the dichlorocarbene addition to $\alpha$-pinene was 15.3 kcal mol$^{-1}$ and proposed an interfacial mechanism. Therefore, this study also gives higher $E_a$ value (i.e., 15.76 kcal.mol$^{-1}$), and hence, it is suggested that dichlorocarbene addition to 1,3-bis(allyloxy)-5-methylbenzene should be proceed through an interfacial mechanism.

![Figure 3. Effect of Temperature](image_url)

**Effect of NaOH concentration**

The reaction rates were measured in the range of 4.41 M - 20.45 M (15 – 45 g NaOH). The $k_{app}$ values of dichlorocyclopropanation strongly depend on the concentration of sodium hydroxide [60]. The $k_{app}$ constants were found to increase with an increase in sodium hydroxide concentration (Fig. 4). This may be attributed to the fact that hydroxide ions are less solvated by water molecules and thereby the activity of the hydroxide ion increases [61]. It is interesting to note that the conversion decreased conspicuously after adding 30 g of sodium hydroxide.
It is because the solution was saturated by the addition of 30 g of sodium hydroxide and 7.89 mmol of 1,3-bis(allyloxy)-5-methylbenzene to 30 mL of water, leading to the salting out of 1,3-bis(allyloxy)-5-methylbenzene as a black gel. Under this circumstance, the dichlorocyclopropanation system would be changing from a liquid–liquid PTC to a liquid–solid (NaOH) PTC. The change would decrease the reaction rate sharply. As shown in Fig. 4, the conversion is first increased with an increase in the amount of NaOH up to 30 g and then decreased with any further increase in the amount of NaOH.

**Figure 4.** Effect of sodium hydroxide

**Mechanism**

Generally, dichlorocarbene addition reaction has been performed in two steps. In the beginning, concentrated sodium hydroxide was treated with chloroform which abstracts a proton and then an intermediate species \( \text{CCl}_3^-\text{Na}^+ \) was generated. Further, it was catalyzed by MPTC and followed by the addition of electrophile: \( \text{CCl}_2 \) (dichlorocarbene). In the phase transfer catalyzed reaction, the two important classes of mechanisms are believed to be operative, viz., Stark’s extraction mechanism [62] in which the hydroxide ion might be extracted from the aqueous reservoir into the organic phase with the help of quaternary onium cations. In the case of Makosza’s interfacial mechanism [63], the abstraction of proton from the organic substrate by the hydroxide ion occurs at inter-face and the resulting organic anion is ferried from the interface into the bulk organic phase by the phase-transfer catalyst for subsequent reaction. In view of these backgrounds,
in our study also it is concluded that the dependence of kinetic data on the [PTC], [NaOH], temperature and higher Ea value and these observation has strongly proved that the reaction may be proceeded through an interfacial mechanism. In the interfacial mechanism, the hydroxide anion first reacted with the chloroform in the organic phase without the help of quaternary onium cations to produce CCl$_3$Na$^+$. Then the anion of MPTC catalyst was exchanged by CCl$_3$Na$^+$ to form an active intermediate of Q$_{2+}$(CCl$_3$)$_2$ which can react with the double bond containing 1,3-bis(allyloxy)-5-methylbenzene to form dichlorocyclopropanated product, viz., 1,3-bis(2,2-dichlorocyclopropyl)methoxy)-5-methylbenzene (Scheme 4). In the presence ultrasonic energy 28 kHz, (300W) the formation of the product increased due to increasing the formation of dichlorocarbene (:CCl$_2$) [64].

**Conclusion**

In this study, a new multi-site phase-transfer catalyst, viz., N,N'-dioctyl-4,4'-bipyridinium dibromide (MPTC) was synthesized and successfully used to carried out a dichlorocarbene addition to new synthesized 1,3-bis(allyloxy)-5-methylbenzene under organic/aqueous bi-phase medium. The reaction is dramatically enhanced by adding a small amount of MPTC along with ultrasonic energy 28 kHz (300W). At a low alkaline concentration, the conversion is low due to less formation of dichlorocarbene. Due to salting out effect the addition of inorganic salt enhances the rate. The proposed interfacial mechanism is well used to explain the reaction behavior.

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