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New soluble multi-site phase transfer catalysts and their catalysis for dichlorocarbene addition to citronellal assisted by ultrasound—A kinetic study

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ABSTRACT

Two new soluble multi-site phase transfer catalysts (MPTCs), viz., 1,4-bis-(triethylmethylene ammonium chloride)-2,5-dimethyl benzene (BTMACD) containing di-site and 1,4-bis((3,5-bis(triethylmethyleneammonium chloride)phenoxy)methyl)benzene (TEMACPB) containing tetra-site were prepared and proved by FT-IR, ^{1}H NMR, ^{13}C NMR, mass and elemental analysis. The enhancement of C—N peak intensity at 1179 cm^{-1} noticed in FT-IR, the agreement of *m*/*z* values, viz., 405 and 888 for di-site and tetra-site respectively with their theoretical values and the percentage of C, H, N elements noticed in elemental analysis has strongly supported the presence of di-site and tetra-site in the BTMACD and TEMACPB catalysts. Further, the presence of number of active-sites in each catalyst was again confirmed by determining their pseudo-first order rate constant for dichlorocarbene addition to citronellal in the presence of ultrasonic irradiation/mechanical stirring. The comparative study reveals that the k_{obs} determined with the combination of ultrasound and mechanical stirring has shown more activity (3 fold) than with their individual effect. Further, the detailed kinetic study performed with superior tetra-site MPTC (TEMACPB) reveals that the k_{obs} are dependent with the stirring speed, [substrate], [catalyst], [NaOH] and temperature. Based on the kinetic results, thermodynamic parameters are evaluated and an interfacial mechanism is proposed.

1. Introduction

Generally, the catalysis researchers have been frequently encountering the inconvenience of conducting a reaction in biphase system. The neutral organic molecule in organic phase and co-reactants in aqueous phase, shows very little tendency to react even at high agitation speed, presence of protic/aprotic solvents and surfactants, due to the shortage of molecular collision. Subsequently, the complication of two immiscible reactants was first rectified by Jarrouse [1] in 1951, by the addition of catalytic quantity of quaternary ammonium salt. Afterwards, several researchers [2–5] had also demonstrated different methods and thus accelerate the rate of reaction in biphasic medium. In 1971, Starks [6] coined the term called "Phase Transfer Catalysis" which meets all the requirements in solving the problems of mutual insolubility of non-polar and ionic compounds. Nowadays, phase transfer catalysis (PTC) is an inevitable potential tool for enhancing the efficiency, improving safety and reducing environmental impact. The advances of the same in the recent years have made a remarkable impact in organic synthesis and are being enormously employed to a multitude of organic transformations such as substitution, displacement, condensation, epoxidation, and polymerization reaction [2]. Even though, various soluble single-site PTCs have extensively used for 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 active site PTC has been immobilized onto the polymer matrices and thus their insoluble heterogeneous single-site phase transfer catalyst are 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 is 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 S_N2 reactions and some weak nucleophile–electrophile SnAr 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

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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-vinylcyclohexne and etherification of 4,4′-bis(chloromethyl)-1,1′-biphenyl and 1-butanol catalyzed by using new soluble MPTC containing two active sites and showed that MPTC exhibits more reactivity than single-site PTC. In our laboratory too, several multi-site phase transfer catalysts are reported for alkylation [13–16], dichlorocarbene addition [17,18], asymmetric synthesis [19–22], decarboxylation [23], functionalization of multi-walled carbon nano tubes [24,25] and polymerization [26] reactions.

Dichlorocarbene addition is an important class of reaction from both industrial and academic perspectives. Dichlorocarbenes are valuable compounds that can be reduced to cyclopropane derivatives, by treating with magnesium or sodium to give allenes and it can be converted to a number of valuable other compounds. The literature surveys stress the necessity for generation and reaction of various dichlorocarbene additions. It is also emphasized that the reaction should carry out only at very strict anhydrous conditions due to its ready and rapid hydrolysis. This problem can be overcome simply by performing the reaction in biphasic system using sodium hydroxide and 'single-site' PTCs [27]. Particularly, if the reaction is performed with "multi-site PTCs" then the rate of the reaction is more, because, the MPTCs generate more dichlorocarbene and thus lead to effective addition to the olefins. In 1969, Makosza and Wawrzyniewicz [28] have first reported 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 [27,29,30].

In recent years, the application of ultrasound irradiation in organic synthesis has been broadly extended. It can increase the rate of reaction, yield and selectivity of desired product under very milder condition [31–34]. Hence, this technique has been considered as a convenient and environmentally benign technique [31,35–40]. 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 transformation [41–46]. The Cannizarro reaction catalyzed by a PTC under ultrasonic condition showed that an ultrasonic wave of 20 kHz dramatically accelerated the rate of reaction [47]. Wang et al. investigated the liquid–liquid phase transfer catalyzed epoxidation and dichlorocyclopropanation of 1,7-octadiene and ethoxylation of p-chloronitrobenzene assisted by ultrasound wave energy, the reaction rates were greatly enhanced in all the reactions [48–50].

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 citronellal using newly synthesized soluble MPTC along with ultrasonic irradiation. Hence, in this study, we have aimed to design and develop two types of new multi-site phase transfer catalysts, viz., 1,4-bis-(triethylmethylene ammonium chloride)-2,5-dimethyl benzene (BTMACD, **3**) having two active site and 1,4-bis((3,5-bis(triethylmethyleneammonium chloride)phenoxy)methyl)benzene (TEMACPB, **7**) containing four active sites through simplified procedures with inexpensive starting materials. Further, the catalytic activity of newly prepared MPTCs and commercial single-site PTCs were studied with dichlorocarbene addition to citronellal under pseudo-first order rate condition in biphasic medium combined with ultrasonic wave energy (42 kHz and 100 W). Further, the catalytically superior tetra-site MPTC was employed for thorough kinetics of dichlorocarbene addition to citronellal and by varying the different experimental parameters such as stirring speed, [substrate], [catalyst], [NaOH] and temperature on the rate of the reaction.

2. Experimental

2.1. Chemicals

The following chemicals were used as received: p-xylene (CDH), paraformaldehyde (Lancaster), Con. HCl (SRL), zinc chloride (SRL), sodium chloride (SDS), 3,5-dimethylphenol (Aldrich), citronellal (Aldrich), N-bromosuccinimide (SRL), N-chlorosuccinimide (SRL), methanol (SRL), benzoylperoxide (SRL), carbon tetrachloride (SRL), acetonitrile (SRL), triethylammine (SRL), chloroform (SRL), hexane (SRL), diethylether (SRL), benzene (SRL), ethyl acetate (SRL), sodium hydroxide (CDH), tetrabutylammonium chloride (TBAC), and benzyltriethylammonium chloride (BTEAC).

2.2. 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 500 MHz and 125 MHz spectrometers. 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 cleaner apparatus (model RZ-08895-22) was used for enhancing the rate of reaction. The kinetics of the dichlorocarbene addition to citronellal 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, chrom WHP 80/100, 3 m × 1/8 in., stainless steel tube.

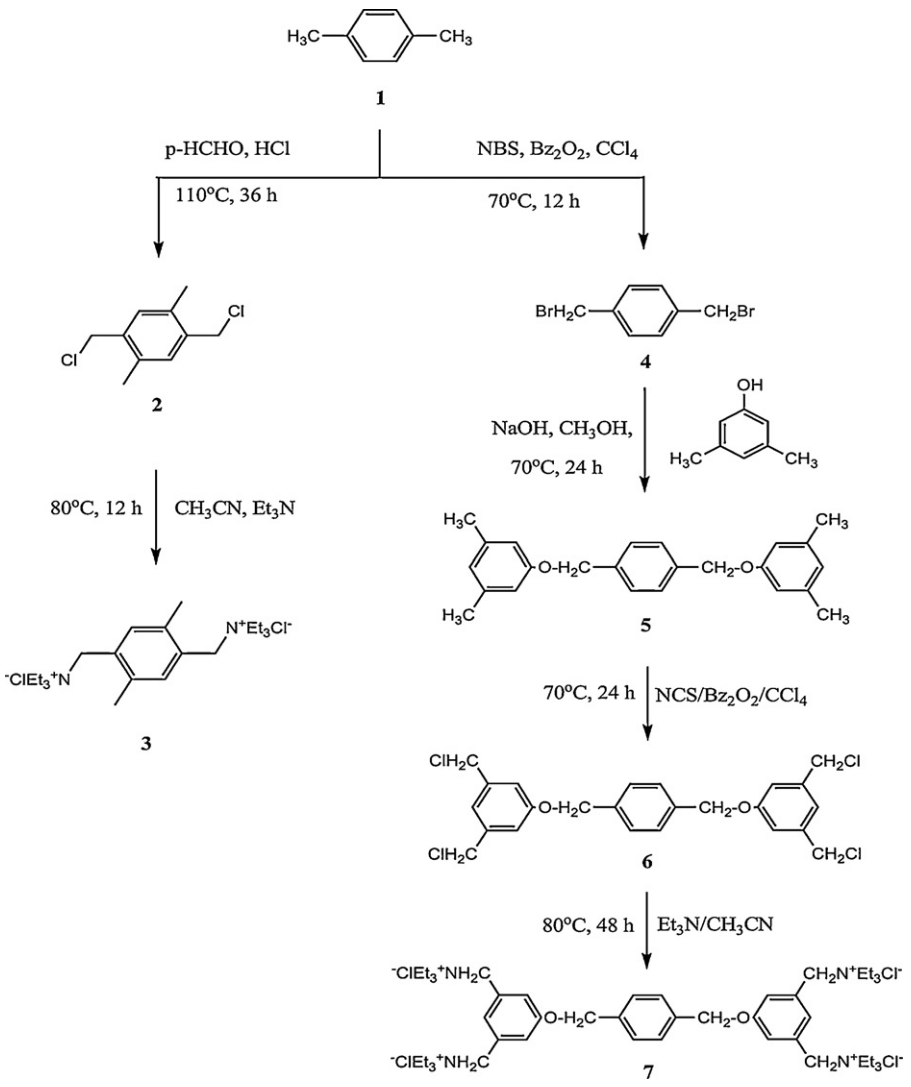
2.3. Synthesis of soluble multi-site phase transfer catalysts (MPTCs) (Scheme 1)

2.3.1. Preparation of di-site PTC, viz., 1,4-bis-(triethylmethyleneammonium chloride)-2,5-dimethyl benzene (BTMACD, 3)

In the first step, the compound **2**, viz., 1,4-bis(chloromethyl)-2,5-dimethyl benzene was prepared by following the simple procedure. That is, p-xylene (3.7 ml; 30 mmol) and conc. HCl (21 ml) were taken in to a 150 ml three necked round bottom flask and it was equipped with a reflux condenser, thermometer and a stirrer. The whole setup was kept on oil bath. Then paraformaldehyde (3.6 g, 120 mmol), zinc chloride (4 g, 30 mmol) and sodium chloride (1 g, 17.11 mmol) were added in to the flask. The whole reaction mixture was refluxed at 110 °C and continuously stirred for 36 h. The resulting white precipitate was filtered and recrystallized using hexane solvent and thus obtained precipitate, viz., 1,4-bis(chloromethyl)-2,5-dimethyl benzene **2** was stored in a desiccator (yield 63% and melting point 102–104 °C, Scheme 1). To confirm the chloromethylation, this product (2) was analyzed with FT-IR and ^{1}H NMR analyses.

FT-IR (KBr, cm^{-1}): 683 (C—Cl stretching), 2977 (aliphatic stretching), 1391 (aliphatic C—H bending); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.408 (s, 6H, —CH_3), 4.586 (s, 4H, —CH_2), 7.176 (s, 2H, Ar—H).

In the second step, 1,4-bis(chloromethyl)-2,5-dimethyl benzene **2** (3 g, 7.39 mmol) was dissolved in dry acetonitrile (25 ml) and then transferred into a 100 ml double necked round bottom flask and the solution was deaerated by passing nitrogen gas. Then, triethylammine (excess) dissolved in acetonitrile (25 ml) was added to that. The reaction mixture was refluxed at 80 °C and stirred for 12 h under the nitrogen atmosphere and thus a white precipitate of quaternized product of di-site PTC, viz., 1,4-bis-(triethylmethyleneammonium chloride)-2,5-dimethyl



Scheme 1. Synthesis of di-site BTMACD and tetra-site TEMACPB catalysts.

benzene (BTMACD, **3**) was obtained. Then the precipitate was filtered and washed with ether solvent (3 × 10 ml) and stored in $CaCl_2$ desiccators. The yield was 85% (Scheme 1).

FT-IR (KBr, cm^{-1}): 1179 (C—N stretching), 2984 (aliphatic C—H str.), 1393 (aliphatic C—H bending); ^{1}H NMR (500 MHz, D_2O): δ 2.396 (s, 6H, —CH_3), 1.278–1.306 (t, 18H, —CH_3), 3.264–3.306 (q, 12H, —CH_2—), 4.423 (s, 4H, —CH_2—), 7.340 (s, 2H, aromatic); ^{13}C NMR (125 MHz, D_2O): δ 7.510, 18.902, 53.419, 58.207; 128.657, 136.284. 138.174; MS [m/z] = 405.15. Elemental Analysis: Calc.: C, 65.16; H, 10.44; N, 6.91. Found: C, 64.95; H, 10.23; N, 6.71.

2.3.2. Synthesis of tetra-site PTC, viz., 1,4-bis-((3,5-bis(triethylmethyleneammonium chloride)phenoxy)methyl)benzene (TEMACPB, ***7****)*

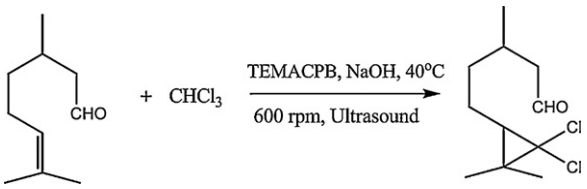
2.3.2.1. Synthesis of 1,4-bis(bromomethyl)benzene ***4****.* In a 250 ml round bottom flask p-xylene **1** (5 ml, 40.78 mmol), and 70 ml of carbon tetrachloride were taken and then the flask was kept on an oil bath. N-bromosuccinimide (29.86 g, 167.80 mmol) and benzoyl peroxide (5.83 g, 24.08 mmol) were added into the flask and the whole solution was refluxed for 12 h at 70 °C. After the completion of reaction, the solution was cooled to room temperature and thus formed solid imide which in turn was removed by filtration. From the filtrate, the solvent was eliminated by distillation to give the pale yellow solid, viz., 1,4-bis(bromomethyl)benzene **4**. The yield was 90% and the melting point was 142–144 °C.

FT-IR (KBr, cm^{-1}): 568 (C—Br), 1625 (C=C); ^{1}H NMR (300 MHz, $CDCl_3$): 4.28 (s, 4H, methylene), 7.182 (s, 4H, aromatic).

2.3.2.2. Synthesis of 1,4-bis-((3,5-dimethylphenoxy)methyl)benzene ***5****.* 1,4-Bis(bromomethyl)benzene **4** (3 g, 11.37 mmol), 3,5-dimethylphenol (2.78 g, 22.74 mmol), methanol (60 ml) and NaOH (0.5 g, 12.5 mmol) were taken in a 250 ml round bottom flask. The reaction mixture was refluxed in an oil bath at 70 °C for 24 h. Then the solvent was removed from the reaction mixture by vacuum evaporator. The condensed product, viz., 1,4-bis-((3,5-dimethylphenoxy)methyl)benzene **5** was obtained. This product was purified by silica gel column chromatography using benzene: ethyl acetate (80:20, v/v). The yield was 69%, melting point was 123–125 °C.

FT-IR (KBr, cm^{-1}): 1075 (C—O), 1614(C—C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.391 (s, 12H, methyl), 5.257 (s, 4H, phenoxymethylene), 7.145–7.819 (m, 10H, aromatic).

2.3.2.3. Synthesis of 1,4-bis((3,5-bis(chloromethyl)phenoxy)methyl) benzene ***6****.* In a 250 ml round bottom flask 1,4-bis-((3,5-dimethylphenoxy)methyl)benzene **5** (3 g, 8.66 mmol),



Scheme 2. Dichlorocarbene addition to citronellal using TEMACPB.

N-chlorosuccinimide (6.02 g, 44.93 mmol), benzoylperoxide (7 g, 28.89 mmol) and carbon tetrachloride were taken and kept in an oil bath. The reaction mixture was refluxed for 12 h at 70 °C. After the completion of reaction time, the solution was cooled and the formation of imide was filtered. The filtrate containing CCl_4 solvent was removed by vacuum evaporator. The crude yellow color product, viz., 1,4-bis((3,5-bis(chloromethyl)phenoxy)methyl)benzene **6** was obtained. The yield was 78% and melting point was 134–136 °C.

FT-IR (KBr, cm^{-1}): 700 (C—Cl), 1073 (C—O); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.728 (s, 8H, methylene), 5.264 (s, 4H, phenoxymethylene), 7.846–8.367 (m, 10H, aromatic).

2.3.2.4. Synthesis of 1,4-bis((3,5-bis(triethylmethyleneammonium-chloride)phenoxy)methyl)benzene (TEMACPB 7). In a 100 ml double necked round bottom flask, 1, 4-bis((3,5-bis(chloromethyl)phenoxy)methyl)benzene **6** (2 g, 2.25 mmol) dissolved in dry acetonitrile (50 ml) was taken. The solution was deaerated by passing nitrogen gas. Then the excess of triethylammine (25 ml) dissolved in acetonitrile was added into the flask. The solution was refluxed at 80 °C for 24 h under inert atmosphere. Then the excess solvent and unreacted triethylammine were removed from the reaction mixture by vacuum evaporator. The obtained white color precipitate of quaternized compound, viz., 1,4-bis((3,5-bis(triethylmethyleneammonium chloride)phenoxy)methyl)benzene (TEMACPB, 7) was filtered, then washed with diethylether (3× 10 ml), dried and stored in a $CaCl_2$ desiccator's. The obtained yield was 72% (Scheme 1).

FT-IR (KBr, cm^{-1}): 1074 (C—O), 1178 (C—N); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.342–1.360 (t.36H, $-N^+CH_2$-methyl), 3.063–3.089 (q, 24H, N^+-methylene), 4.658 (s, 8H, methylene), 5.278 (s, 4H, phenoxymethylene), 8.045–8.786 (m, 10H, aromatic), ^{13}C NMR (125 MHz, $CDCl_3$): δ 8.46, 53.03, 61.56, 66.83, 119.20, 127.28, 129.43, 130,73, 132.52, 146.71. MS (m/z) = 888.12. Elemental Analysis: C, 64.85; H, 9.30; N, 6.30. Found: C, 64.68; H, 9.06; N, 6.12.

2.4. Kinetics of dichlorocarbene addition to citronellal

The kinetics of the reaction was performed in an ordinary 150 ml three-necked round bottom flask fitted with flat-bladed stirring paddle and a reflux condenser. The dichlorocarbene addition of citronellal reaction was carried out by reverse addition method, i.e., by delayed addition of citronellal (Scheme 2). Into the reaction flask, 25 ml of (20%, w/w) aqueous NaOH, 0.23 mmol of respective catalyst and 20 ml chloroform (solvent) were added and stirred at 200 rpm for 5 min at 40 °C to stabilize the catalyst. Citronellal (1.0 ml, 5.58 mmol) preheated to 40 °C was added to the reaction mixture at zero time. The reaction mixture was stirred at 600 rpm and simultaneously the ultrasonic wave energy (42 kHz and 100 W) was 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 seven samples. The kinetics of the reaction was followed by estimating the amount of citronellal disappeared using gas chromatograph. The temperature of the column was maintained at 200 °C. An aliquot of reaction mixture (0.5 μl) was injected into the column and the product was analyzed. The retention time for each compound was noted such as citronellal (1.14 min), chloroform (0.71 min), and dichlorocyclopropane product (4.50 min). The pseudo-first order rate constants were calculated from the plots of log (a–x) versus time. The kinetic experiments were carried out in duplicate to confirm reproducibility of the results.

3. 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 to replace the low active single-site PTC. Particularly, dichlorocarbene addition to olefin using MPTCs aided by ultrasonic wave energy is an active area for current study. To strengthen further, two different new soluble MPTCs such as di-site PTC, viz., 1,4-bis-(triethylmethylene ammonium chloride)-2,5-dimethyl benzene (BTMACD, **3**) and tetra-site PTC, viz., 1,4-bis((3,5-bis(triethylmethyleneammonium chloride)phenoxy)methyl)benzene (TEMACPB, **7**) were prepared by adopting the simplified procedures. The availability of number of quaternary ammonium groups (catalytic-site) in each catalyst was established with FT-IR, ^{1}H NMR, ^{13}C NMR, mass, and elemental analyses. The structure of di-site (**3**) and tetra-site (**7**) MPTCs were confirmed by the disappearance of C—Cl stretching at 700 cm^{-1} and appearance of C—N stretching at 1179 cm^{-1} in FT-IR spectrum. However, the number of quaternary onium group present in each catalyst was estimated semiquantitatively through comparative FT-IR study. The comparative FT-IR studies obtained from single-site (BTEAC) to tetra-site (TEMACPB) reveals that the C—N peak intensity at 1179 cm^{-1} has been gradually increased from BTEAC (single-site) to TEMACPB (tetra-site) and it proves the presence of more number of quaternary onium groups in BTMACD (di-site) and in TEMACPB (tetra-site) catalysts. In the ^{1}H NMR analysis, the quaternized ethyl group consisting of methyl and methylene proton appeared as triplet and quartet at 1.278–1.306 ppm and 3.264–3.306 ppm respectively for di-site and 1.342–1.360 and 3.063–3.089 ppm respectively for tetra-site and thus supporting the formation of quaternizing groups. Similarly, in ^{13}C NMR, the methyl and methylene carbon showed high intense peaks at 7.510 and 53.419 ppm respectively for di-site and 8.46 and 53.03 ppm respectively for tetra-site, thus strongly supported the formation of quaternizing sites. Further, in mass analysis the experimentally found m/z values, i.e., 405 for di-site and 888 for tetra-site were agreed well with their theoretical values. In the case of elemental analysis, the percentage of C, H, N elements determined experimentally were found to agree with their theoretical values irrespective of catalyst and thus strongly supported the presence of di-site in BTMACD (**3**) and tetra-site in TEMACPB (**7**) catalysts. On the other hand, although the number of quaternary onium groups (active sites) in each catalyst was proved beyond doubt through various techniques, but again its presence in the respective catalyst should also be confirmed through catalytic activity. To determine the catalytic activity of these newly synthesized soluble MPTCs, they were employed individually for the catalysis of dichlorocarbene addition to citronellal under identical pseudo-first order reaction conditions in association with ultrasonic irradiation (42 kHz, 100 W) and mechanical stirring. The pseudo-first order rate constant was determined by measuring the disappearance of citronellal under regular intervals using gas chromatography.

3.1. Comparative catalytic study of newly developed MPTCs, viz., BTMACD and TEMACPB with known single-site PTCs

In order to investigate the number of quaternary onium groups (active-site) available in newly synthesized di-site viz., 1,4-bis-(triethylmethylene ammonium chloride)-2,5-dimethyl benzene (BTMACD, **3**) and tetra-site, viz., 1,4-bis((3,5-bis(triethylmethyleneammonium chloride)phenoxy)methyl)benzene (TEMACPB, **7**), the pseudo-first order rate constants (k_{obs}) for the dichlorocarbene addition to citronellal was determined and the same was compared with the rate constant determined with two different known (commercial) single-site PTCs, viz., benzyltriethylammonium chloride (BTEAC) and tetrabutylammonium chloride (TBAC). Of course, as it was mentioned in the experimental section, the reaction was performed under identical experimental conditions irrespective of the catalyst and in the presence of ultrasound wave energy of 42 kHz (100 W). From the obtained result (Table 1), it infers that the k_{obs} was increased on par with number of quaternary onium groups available in each catalyst (molecule). That is, the activity lies in the order of BTEAC (single-site) < TBAC (single-site) < BTMACD (di-site) < TEMACPB (tetra-site) irrespective of reaction performed in mechanical stirring, ultrasonic wave energy and combination of both.

To describe elaborately, the k_{obs} determined individually with the help of ultrasonic wave energy and mechanical stirring (Table 1) reveals that in both the cases, the di-site and tetra-site has shown approximately 2 and 4 times higher active than that of single-site PTCs. Similarly, in the case of combination of ultrasonic irradiation and mechanical stirring, the k_{obs} for di-site MPTC and tetra-site MPTC shows approximately 2.5 and 5 times higher active than that of BTEAC single-site PTC. This observation has strongly supported that the number of quaternary onium groups present in each catalyst has contributed directly to the reaction and thus in turn reflected in activity. Further, on comparing the k_{obs} determined with mechanical stirring and ultrasonic irradiation, the mechanical stirring has influenced the reaction more effectively than the ultrasonic irradiation. Furthermore, the comparative study reveals that the k_{obs} determined with the combination of ultrasound and mechanical stirring has shown 3 fold more activity than with their individual effect. The previously reported studies reveal that the presence of ultrasonic wave energy increases the collision rate between the reactants which are present in the organic and aqueous phase and decrease the surface area between the two layers [51]. We have already reported similar observation [13–18,26].

Generally, the effect of ultrasonic irradiation for the promotion of dichlorocarbene addition to citronellal 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 [52–55]. 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 cavitational collapse near the liquid–liquid interface and impels jets of one liquid into other, forming fine emulsions and it leads to a dramatic enhancement in the interfacial contact area through which transfer of species can take place [56]. Therefore, the combination of quaternary onium ions (PTC) and ultrasound energy has proved to be a best and environmentally benign catalytic method to conduct the organic addition reaction [57,58]. In view of the impact of ultrasonic wave energy, it is decided to conduct detailed kinetic study for dichlorocarbene addition to citronellal using the superior tetra-site MPTC, viz., TEMACPB in association with ultrasonic wave energy and by varying the experimental parameters such as stirring speed, [substrate], [MPTC], [NaOH], and temperature.

Table 1
Comparative catalytic study of newly developed MPTCs, viz., BTMACD and TEMACPB with known single-site PTCs: 5.58 mmol of citronellal, 25 ml of NaOH (20%, w/w), 20 ml of chloroform, 0.23 mmol of PTC, 40 °C, 600 rpm, under ultrasound conditions (42 kHz, 100 W).

Catalysts	$k_{obs} \times 10^3$ (min^{-1})		
	Ultrasound only	Stirring only	Stirring with ultrasound
BTEAC	1.48	1.96	5.14
TBAC	1.67	2.16	5.82
BTMACD	2.93	3.98	11.79
TEMACPB	6.12	8.25	24.37

3.2. Effect of varying the stirring speed

With a view to study the effect of stirring speed on the rate of dichlorocarbene addition to citronellal using new tetra-site MPTC, viz., TEMACPB, the reaction was studied by varying the stirring speed in the range of 100–800 rpm along with ultrasonic irradiation. The other parameters such as [substrate], [catalyst], [NaOH] and temperature were kept constant. The pseudo first order rate constants were evaluated from the plots of log(a–x) versus time (Fig. 1). From the observed k_{obs}, it is understood that the rate of the reaction increases on increasing the stirring speed, i.e., the rate constant was gradually increased from 100 to 400 rpm and then sharply increased to 500 rpm and then reaches a maximum at 600 rpm. Further, the rate constant of the reaction was not improved on increasing the stirring speed above 600 rpm. Similar trend of observation is already reported in effect of varying the stirring speed [2,3,59,60] and it was suggested that the reaction has followed interfacial mechanism. Similarly, Starks et al. [1] reported analogue behavior displayed by reactions with a real 'phase transfer' (Stark's extraction mechanism); there is much smaller limit of stirring speed between physical and chemical control (100–300 rpm). Therefore, based on the k_{obs} trend noticed in stirring speed, it is suggested that the reaction kinetics is controlled by the chemical reaction in the organic phase for stirring speed at above 600 rpm. Further, at stirring rate of 600 rpm, there is a rapid anion exchange equilibrium which is relative to the organic displacement reaction. From the 100 to 400 rpm, the requirement for the adequate mass transfer of the reaction anion was not found and diffusion controlled kinetics was observed, but at 500 rpm there was a sharp increase in the k_{obs} and this is due to the "effective mass transfer" of reactant from aqueous phase to organic phase. This kind of observation was reported earlier by Landini et al. [61] in the study of n-octylmethane sulfonate catalyzed by quaternary salts

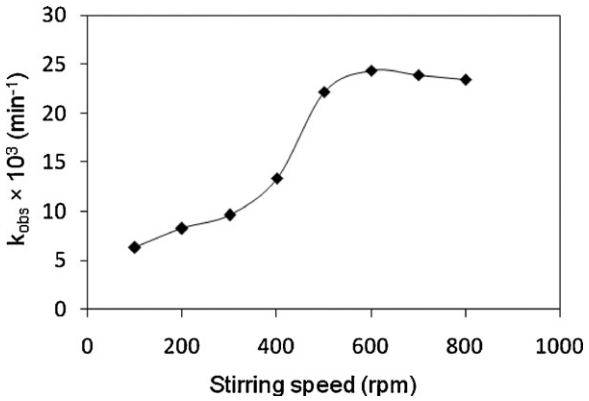


Fig. 1. Effect of stirring speed: 5.58 mmol of citronellal, 25 ml of NaOH (20%, w/w), 20 ml of chloroform, 0.23 mmol of TEMACPB, 40 °C, under ultrasound conditions (42 kHz, 100 W).

Q^+X^- under the PTC condition in a chlorobenzene–water biphasic medium. Balakrishnan et al. [8,62] reported the same trend in dichlorocarbene addition to styrene and in the study of C-alkylation of phenylacetone using ethyl iodide. Wang et al. [11,63] observed a similar behavior in the kinetic study of dichlorocyclopropanation of 4-vinyl-1-cyclohexene and in the dichlorocarbene addition to allyl phenyl ether and proposed an interfacial mechanism. Recently, Murugan et al. [16] also reported the similar trend of observation in the C-alkylation of dihydrocarvone reaction in which the rate of the reaction increased up to 600 rpm and at above 600 rpm the rate constant reaches constant. In the present study also, k_{obs} is independent of the stirring speed at above 600 rpm, and this trend indicates that the reaction has proceeded through interfacial mechanism. Hence, the stirring speed was set as an optimum at 600 rpm for further kinetic experiments.

3.3. Effect of [substrate]

The effect of varying the concentration of citronellal on the rate of dichlorocarbene addition was studied in the range of 2.79–13.94 mmol and keeping the other reagents as constant under the ultrasonic irradiation condition. From the plot of log(a–x) versus time, the pseudo-first order rate constants were evaluated (Table 2, Fig. 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 MPTC and higher concentration of substrate had co-operatively influenced the reaction and thus enhanced the more number of contacts between catalyst and substrate and hence reflected in enhanced k_{obs}. Balakrishnan et al. reported similar results in the study of C-alkylation of phenylacetone [62] and phenylacetonitrile [8] with n-bromobutane using PTC. Recently, Murugan et al. [14,18] have also reported the same dependency of rate constants for the dichlorocarbene addition to citral and α-pinene using MPTC.

Table 2
Effect of [substrate] on k_{obs}: 25 ml of NaOH (20%, w/w), 20 ml of chloroform, 0.23 mmol of TEMACPB, 40 °C, 600 rpm, under ultrasound conditions (42 kHz, 100 W).

[Citronellal] mmol	$k_{obs} \times 10^3$ (min^{-1})	log [citronellal]	$3 + \log k_{obs}$
2.79	14.21	0.4456	1.1709
5.58	24.37	0.7466	1.3869
8.36	30.19	0.9222	1.4799
11.15	34.68	1.0473	1.5401
13.94	39.33	1.1443	1.5947

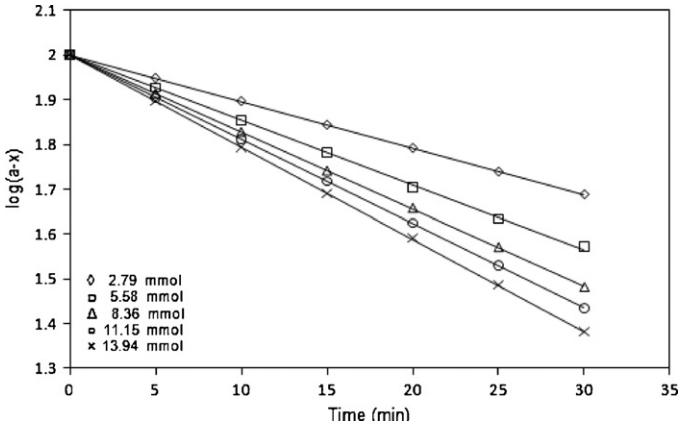


Fig. 2. Effect of [substrate] on k_{obs}: 25 ml of NaOH (20%, w/w), 20 ml of chloroform, 0.23 mmol of TEMACPB, 40 °C, 600 rpm, under ultrasound conditions (42 kHz, 100 W).

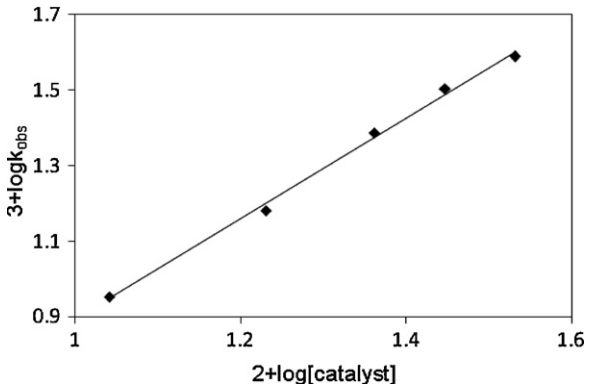


Fig. 3. Effect of [catalyst] on k_{obs}: 5.58 mmol of citronellal, 25 ml of NaOH (20%, w/w), 20 ml of chloroform, 40 °C, 600 rpm, under ultrasound conditions (42 kHz, 100 W).

3.4. Effect of [catalyst]

The effect of variation of [catalyst] on the rate of the dichlorocarbene addition to citronellal was studied in the range of 0.11–0.34 mmol of the MPTC, viz., TEMACPB and keeping the other experimental parameters as constant under the ultrasonic irradiation condition. The pseudo-first order rate constants were evaluated from the plot of log(a–x) versus time (Fig. 3). From the observed results, the rate constants are linearly dependent on the concentration of catalyst. The increased rate constants are attributed to increase in number of catalytic active site which in turn enhance the more number of effective collisions between $Na^+CCl_3^-$ and $N^+Et_3Cl^-$ (active site) in the interface. In other words, at higher concentration of $N^+Et_3Cl^-$, the generation of:CCl_2 have been increased which in turn leads to increase in the formation of complex between $N^+Et_3Cl^-$ and:CCl_2 in the organic phase. Further, not only higher rate of reactions were obtained due to the presence of more amount of catalyst but also intensification of the rate had occurred [64] and also there was a total suppression of side reactions leading to 100% selectivity of the product. The control experiments were also carried out for dichlorocarbene addition to citronellal, negligible amount of product was formed even after 3 h of reaction. The linear dependence of the reaction rate constants on [catalyst] shows that the reaction is believed to proceed through the interfacial mechanism. The bi-logarithmic 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 [65] in the study of dichlorocarbene addition to cyclohexene using tridecylmethylammonium chloride as catalyst. Halpern et al. [66] 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 effect of catalyst structure was studied by Dehmlow's [27] in the dichlorocarbene addition to cyclohexene and reported the higher yield.

3.5. Effect of [NaOH]

The rate of the dichlorocarbene addition strongly depends on the concentration of NaOH. In the presence of aqueous NaOH, the dichlorocarbene is generated by the abstraction of proton from chloroform and further it reacts with substrate present in the organic phase to give the desired product. Hence, the rate of dichlorocarbene addition has strongly accelerated by the concentration of alkali in aqueous solution. The effect of [NaOH] on the rate of dichlorocarbene addition to citronellal was

Table 3
Effect of [NaOH] on k_{obs}: 5.58 mmol of citronellal, 20 ml of chloroform, 0.23 mmol of TEMACPB, 40 °C, 600 rpm, under ultrasound conditions (42 kHz, 100 W).

% of NaOH (w/w)	[NaOH] (M)	$k_{obs} \times 10^3$ (min^{-1})	log [NaOH]	$3 + \log k_{obs}$
10	2.78	7.22	0.4440	0.8588
15	4.41	13.89	0.6444	1.1427
20	6.25	24.37	0.7959	1.3869
25	8.33	32.66	0.9206	1.5140
30	10.71	44.65	1.0298	1.6498

studied by varying [NaOH] from 2.78 to 10.71 M and keeping other parameters as constant under the ultrasonic irradiation condition. From the observed experimental results, the rate constant has been increased on increasing the concentration of NaOH (Table 3, Fig. 4). The main reason is that at higher [NaOH], hydroxide ions are less solvated by water molecules and thereby the activity of hydroxide ion is increased. Further, under this condition the hydrolysis of dichlorocarbene is also minimized which in turn facilitates the reaction. A bilogarithmic plot of the reaction rate against [NaOH] gives a straight line with a slope of 0.96. Balakrishnan and Jayachandran [8] observed the same trend with quaternary onium salts.

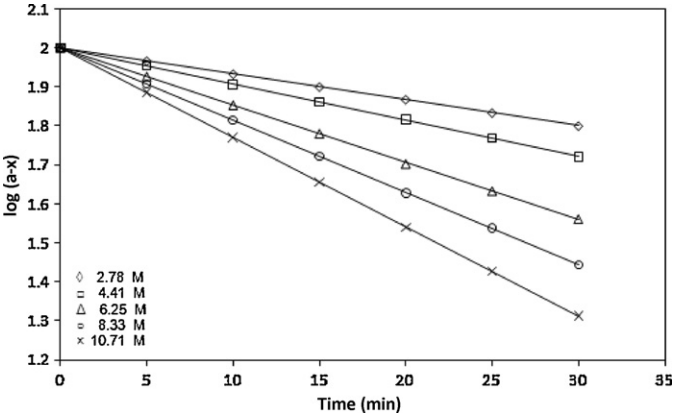
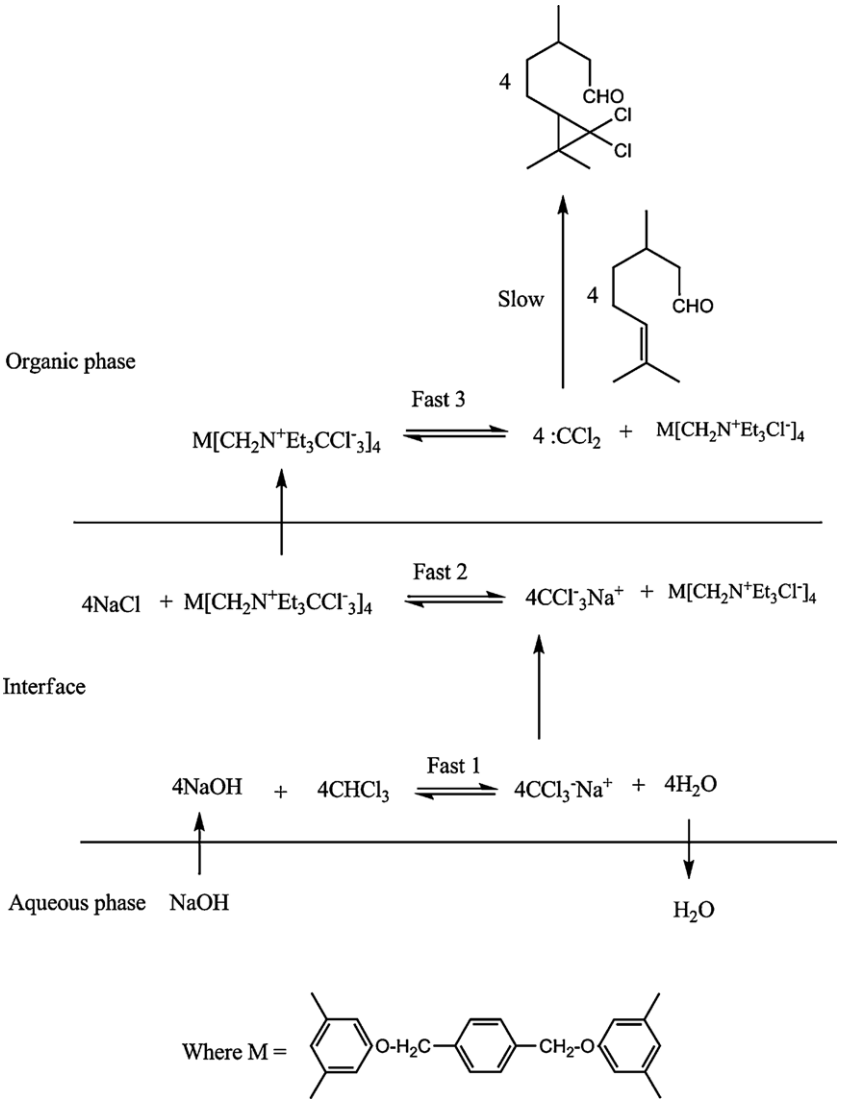


Fig. 4. Effect of [NaOH] on k_{obs}: 5.58 mmol of citronellal, 20 ml of chloroform, 0.23 mmol of TEMACPB, 40 °C, 600 rpm, under ultrasound conditions (42 kHz, 100 W).

3.6. Effect of temperature

The effect of varying the temperature on the rate of dichlorocarbene addition to citronellal was carried out in the temperature



Scheme 3. Interfacial mechanism for dichlorocarbene addition to citronellal.

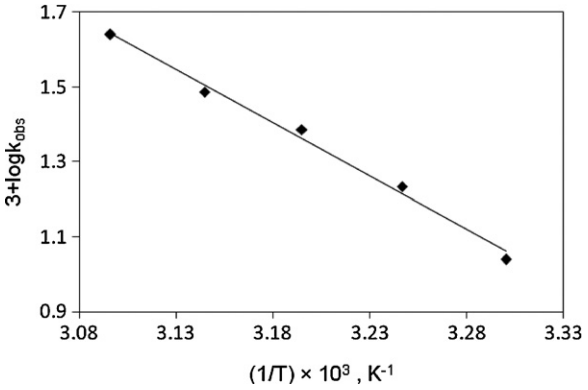


Fig. 5. Arrhenius plot: effect of temperature on k_{obs}: 5.58 mmol of citronellal, 25 ml of NaOH (20%, w/w), 20 ml of chloroform, 0.23 mmol of TEMACPB, 600 rpm, under ultrasound conditions (42 kHz, 100 W).

range of 303–323 K and keeping the other experimental parameters as constant under the ultrasonic irradiation condition. The pseudo-first order rate constants were evaluated from the plot of log(a–x) versus time (Fig. 5). The observed values indicate that the reaction rate constants were increased on increasing the temperature in association with ultrasonic wave energy [67]. The energy of activation is calculated from Arrhenius plot (Fig. 5), E_a = 15.76 kcal mol^{-1}. The other thermodynamic parameters such as entropy of activation ($\Delta S^{\#}$), enthalpy of activation ($\Delta H^{\#}$) and free energy of activation ($\Delta G^{\#}$) for dichlorocarbene addition to citronellal were determined from Eyring's equation and the obtained values are −14.7 kcal^{-1} mol^{-1}, 15.1 kcal mol^{-1} and 16.9 kcal mol^{-1} respectively.

The activation energy (E_a) reported by Chiellini et al. [68] for ethylation of phenylacetonitrile was 20 kcal mol^{-1} and for this an interfacial mechanism was proposed. Reeves and Hilbrich [60] 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 [69] observed a higher E_a value for the polystyrene bound triethylammonium ion catalyzed reaction, which was controlled by strict 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. Recently, Murugan et al. [18] reported the higher E_a value for the dichlorocarbene addition to α-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 citronellal should be proceed through an interfacial mechanism.

3.7. Mechanism

Generally, in 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 $CCl_3^-Na^+$ was generated. Further, it was catalyzed by MPTC and followed by the addition of electrophile. In the phase transfer catalyzed reaction, the two important classes of mechanisms are believed to be operative, viz., Stark's extraction mechanism [70] 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 [71], the abstraction of proton from the organic substrate by the hydroxide ion occurs at interface and the resulting organic anion is ferried from the interface into the bulk organic phase by the phase transfer catalyst for subsequent reaction. In interfacial mechanism, the addition of:CCl_2 to alkene is the slowest reaction, considering the other steps as fast equilibrium processes. In view of these backgrounds, in our study also it is concluded that the dependence of kinetic data on the stirring speed, [catalyst], [NaOH], temperature and higher E_a 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 MPTC/CCl_3^- which can react with the double bond containing citronellal to form dichlorocyclopropanated product, viz., 5-(2,2-dichloro-3,3-dimethylcyclopropyl)-3-methylpentanal (Scheme 3).

4. Conclusion

New soluble multi-site phase transfer catalysts, viz., 1,4-bis-(triethylmethylene ammonium chloride)-2,5-dimethyl benzene (BTMACD) with two active sites and 1,4-bis((3,5-bis (triethylmethyleneammonium chloride)phenoxy)methyl)benzene (TEMACPB) having four active sites were prepared from inexpensive starting material by adopting the simplified procedures. The presence of active sites in BTMACD and TEMACPB catalyst was confirmed by FT-IR, ^{1}H NMR, ^{13}C NMR, mass and elemental analysis techniques. Especially, in FT-IR studies, the C—N peak intensity noticed at 1179 cm^{-1} has been increased from BTEAC (single-site) to TEMACPB (tetra-site) and thus suggests the enhancement of number of quaternary onium group. Similarly, in ^{1}H NMR analysis, the quaternized *N*-ethyl group containing of methyl and methylene proton peaks appeared as triplet and quartet at 1.34 and 3.06 ppm respectively and in ^{13}C NMR, the methyl and methylene carbon has shown high intense peak at 8.46 and 53.03 ppm respectively, these results has confirmed the formation of active site in the respective MPTC. Further, in mass and elemental analyses, the observed experimental values are almost equal with that of theoretical value, and they have strongly supported the presence of number of quaternary onium groups. Further, the catalytic efficiency of newly prepared MPTCs and known single-site PTCs were ascertained from the rate of dichlorocarbene addition to citronellal individually with ultrasonic irradiation/mechanical stirring and also with combination of both. That is, in the comparative study, the k_{obs} determined by ultrasonic wave energy/mechanical stirring and combination of both, were found in the order of BTEAC (single-site) < TBAC(single-site) < BTMACD (di-site) < TEMACPB (tetra-site), and thus in turn proves the number of quaternary onium groups in the respective MPTCs. Similarly, the k_{obs} determined with ultrasonic wave energy/mechanical stirring reveals that, in both cases, di-site and tetra-site MPTC has shown 2 and 4 fold more active than single-site PTC. Similarly, in the case of combination, the k_{obs} for di-site and tetra-site MPTC has shown 2.5 and 5 fold more active than that of BTEAC single-site PTC and thus it confirms the presence of number of quaternary onium groups in the respective MPTC. Further, the superior tetra-site MPTC, viz., TEMACPB has been studied for the thorough kinetics of dichlorocarbene addition to citronellal. The rate of reaction increased on increasing the stirring speed, [substrate], [catalyst], [NaOH], and temperature. Furthermore, the activation energy E_a and other thermodynamic parameters such as entropy of activation ($\Delta S^{\#}$), enthalpy of activation ($\Delta H^{\#}$), and free energy of activation ($\Delta G^{\#}$) values were also evaluated. From the observed kinetic results, it is apparent that the reaction follows an interfacial reaction mechanism.

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