Journal of Molecular Catalysis A: Chemical 294 (2008) 68–73

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Catalytic activity of novel soluble multi-site phase transfer catalyst in dichlorocarbene addition to α-pinene

Eagambaram Murugan*, Prakash Gopinath

Department of Physical Chemistry, School of Chemical Sciences, University of Madras, Guindy Campus, Chennai 600025, Tamil Nadu, India

ARTICLE INFO

Article history:
Received 29 May 2008
Received in revised form 6 August 2008
Accepted 7 August 2008
Available online 19 August 2008

Keywords:
MPTC
Dichlorocarbene addition
α-pinene
Interfacial mechanism

ABSTRACT

A novel soluble multi-site phase transfer catalyst (MPTC), viz., 2,4,6-tris(triethylammoniummethylene chloride) mesitylene (TTEAMCM) containing three active sites was synthesized and characterized through FT-IR, ^{1}H NMR, ^{13}C NMR and [chloride ion] analyses. The spectral and [chloride ion] results strongly confirm the presence of three active sites in the catalyst. The catalytic efficacy of this new soluble MPTC was examined by determining the pseudo-first order rate constant for dichlorocarbene addition to α-pinene reaction using low concentration of NaOH (20%) at 40 °C and comparing the observed rate constant with the rate constant of the same reaction catalyzed by commercially available single-site PTCs under identical reaction conditions. The observed result shows that TTEAMCM has a higher reactivity (≈threefold) than the single-site PTCs in terms of rate constant. Further, a thorough kinetic study was conducted for dichlorocarbene addition to α-pinene using TTEAMCM by varying the experimental parameters such as stirring speed, [substrate], [NaOH], [catalyst] and temperature and it was found that the rate constants show dependence on all the experimental parameters. The activation energy and thermodynamic parameters viz., enthalpy, entropy and free energy change were also calculated. Based on the observed kinetic and thermodynamic parameters, an interfacial mechanism was proposed for dichlorocarbene addition to α-pinene.

1. Introduction

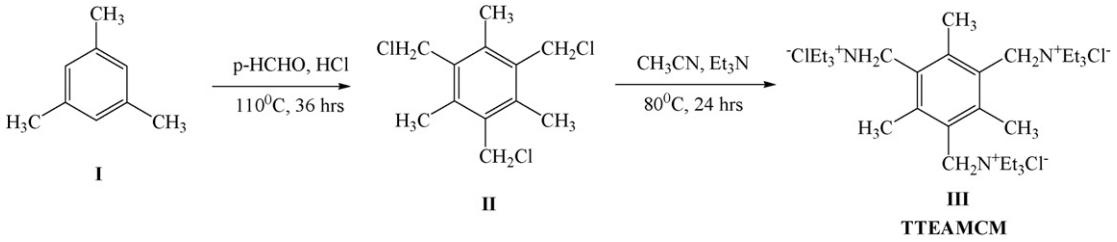
Phase transfer catalysis is a versatile, well established synthetic technique applicable to a number of organic bi-phase reactions [1–3]. This technique has become one of the most interesting and fascinating topics of research during the last few years [4–6] being successful for a multitude of organic transformations. Several soluble and insoluble forms of single-site phase transfer catalysts are already available commercially, but their utilities are limited owing to their low efficiency in the reactions. Particularly, some of the medically valuable products and intermediates are obtainable only through high energy reaction conditions like high energy input or high concentration of catalyst, that too with low yield. Preference for phase transfer catalyst (PTC) arise from factors like low economy, high efficiency and low energy requirements. Hence, many studies are reported on attempts to develop multi-site phase transfer catalysts (MPTCs) containing more than one catalytic active site in a molecule. This type of MPTCs offer the potential of providing greater PTC activity and accelerating the particular synthetic transformation even under mild conditions.

Idoux et al. [7] were the first to synthesize MPTCs containing three phosphonium active sites in both soluble and insoluble polymer-supported forms. The catalytic activities of these MPTCs towards simple S_N2 reaction and some weak nucleophile–electrophile S_NAr reactions were also reported. Balakrishnan and Ford [8] reported soluble ammonium PTCs containing two and three active sites. Recently, Wang and Hsieh [9] performed the kinetic study of dichlorocyclopropanation of 4-vinyl-cyclohexene using a new di-site PTC synthesized from dichloro-*p*-xylene. One important salient feature for employing MPTC for any chemical reaction is that the concentration of MPTCs required to conduct the reaction are relatively low compared with soluble single-site PTCs. In our laboratory, we also reported different multi-site PTCs for alkylation reactions [10,11], dichlorocarbene addition [12] and asymmetric synthesis [13–16].

Dihalocarbenes are very useful compounds that can be reduced to cyclopropane derivatives by treating with sodium to give allenes and subsequently can be converted to a number of pharmaceutically valuable products [17]. The dichlorocarbene addition reaction under biphasic conditions was studied by Makosza and Wawrzyniewicz [18] in 1969 using 50% aqueous NaOH and chloroform, a high yield of dichlorocyclopropane product was obtained. Numerous reports were available for the dichlorocarbene addition to various olefins using single-site PTCs [19–21]. The studies on

* Corresponding author. Tel.: +91 44 22202818/22202819; fax: +91 44 22352494.
E-mail address: murugan_e68@yahoo.com (E. Murugan).

1381-1169/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2008.08.004



Scheme 1. Synthesis of soluble tri-site PTC TTEAMCM.

the addition of dichlorocarbene to α-pinene was firstly reported by Arbuzov and coworkers [22] and the dichlorocarbene adduct was synthesized with the yield of 30% as a stable crystal. Julia and Ginebreda [23] reported the use of solid NaOH, TEBAC for the solid–liquid phase transfer catalytic addition of dichlorocarbene to α-pinene. However, there is no report available on the kinetics of dichlorocarbene addition to α-pinene using soluble MPTC. In view of these discussions, we have synthesized a novel soluble MPTC, viz., 2,4,6-tris(triethylammoniummethylene chloride) mesitylene TTEAMCM containing three active sites from inexpensive starting materials. The structure of the MPTC was characterized through FT-IR, ^{1}H NMR and ^{13}C NMR. Further, the concentration of chloride ion present in the catalyst was determined by Volhard's method [24]. The catalytic efficiency of new MPTC was examined by determining the pseudo-first order rate constant for dichlorocarbene addition to α-pinene reaction and comparing the same with the rate constant of the same reaction catalyzed by commercial single-site PTCs. Detailed kinetic study was also performed for dichlorocarbene addition to α-pinene by varying the stirring speed, [substrate], [catalyst], [NaOH] and temperature.

2. Experimental

2.1. Chemicals

The following were used as provided: mesitylene (Lancaster), paraformaldehyde (Lancaster), conc. HCl (SRL), triethylamine (Merck), sodium chloride (Merck), zinc chloride (SRL), ethanol (Merck), chloroform (SRL), acetonitrile (SRL), α-pinene (Fluka), sodium hydroxide (SRL), tetraethylammonium chloride (TEAC), tetraethylammonium bromide (TEAB), benzyltriethylammonium bromide (TEBAB) and benzyltriethylammonium chloride (TEBAC) were used as provided.

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 JEOL 200 MHz and Bruker AR 50 MHz spectrometers respectively. The kinetics of the dichlorocarbene addition to α-pinene was quantitatively analyzed 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. Procedure for preparation of tri-site PTC, viz., 2,4,6-tris(triethylammoniummethylene chloride) mesitylene (TTEAMCM, ***III***) (Scheme 1)

2.3.1. Preparation of 2,4,6-tris(chloromethyl)mesitylene(***II***)

In the first step, the compound **II**, viz., 2,4,6-tris(chloromethyl) mesitylene was synthesized using the procedure reported earlier [25]. In a 250 ml three-necked flask equipped with a reflux condenser, a thermometer and a stirrer are placed. Mesitylene (4.2 ml, 0.03 mol) conc. HCl (21 ml), paraformaldehyde (5.4 g, 0.18 mol), zinc chloride (4.1 g, 0.03 mol) and sodium chloride (0.926 g, 0.016 mol) were added to the flask. The reaction mixture was stirred and refluxed for 36 h. The resulting solid product was rescrystallized using hexane. The melting point of the product is 165 °C, yield 90%.

FT-IR (KBr), cm^{-1}: 2922 (aliphatic C–H), 723 (C–Cl).

^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.38 (s, 9H, methyl), 4.55 (s, 6H, methylene).

2.3.2. Preparation of 2,4,6-tris(triethylammoniummethylene chloride) ***III***

In the second step, 2,4,6-tris(chloromethyl) mesitylene(**II**) (2 g, 0.0075 mol) was dissolved in dry acetonitrile (40 ml) and transferred into a 150 ml RB flask. The solution was deaerated and triethylamine (30 ml) was added to the solution. The reaction mixture was gently refluxed for 24 h under nitrogen atmosphere. Then the solvent was removed by rotary evaporator. The resulting yellow coloured product was recrystallized using ethanol and stored in a desiccator. Yield 87%, decomp. temperature 220 °C.

FT-IR (KBr), cm^{-1}: 1093 (C–N), 1640 (C = C), 2921 (aliphatic C–H).

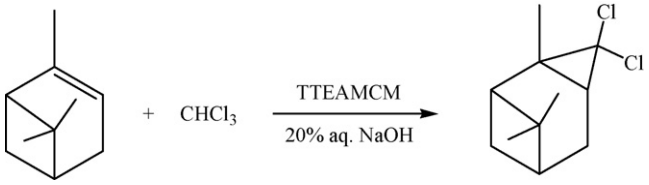
^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.26 (t, 27H, J = 5.0 Hz, –methyl), 2.42 (s, 9H, methyl), 3.31 (q, 18H, J = 6.8 Hz, methylene), 4.67 (s, 6H, methylene).

^{13}C NMR (50 MHz, $CDCl_3$) δ: 7.3, 12.4, 18.2, 57.2, 126.5, 137.7.

[Chloride ion] = 12.3 mequiv. g^{-1} (Volhard's method).

2.4. Typical kinetic experiments

The kinetic experiments were performed in an ordinary 150 ml three-necked flask fitted with a flat-bladed stirring paddle and a reflux condenser. The dichlorocarbene addition to α-pinene reaction (Scheme 2) was carried out by reverse addition method, i.e. delayed addition of chloroform. The substrate α-pinene (1 ml, 6.29 mmol), aqueous NaOH (20%, w/w; 25 ml), hexadecane (1.54 g) and catalyst (3.5×10^{-4} mmol) were taken in the flask and stirred at 300 rpm for 5 min at 40 °C to condition the catalyst. The stirring speed was increased to 500 rpm and 20 ml of chloroform was added at zero time. Samples were collected from the organic layer of the mixture (by stopping the stirring for 10–15 s each time) at regular intervals. Each run consists of seven samples taken over the period ranging from 5 to 35 min. The kinetics was followed by



Scheme 2. Dichlorocarbene addition to α-pinene using TTEAMCM.

estimating the amount of α-pinene that disappeared using a gas chromatograph. The temperature of the column was maintained at 150 °C. An aliquot of reaction mixture (0.5 μl) was injected into the column and the products were analyzed. The retention time for each compound is given within the brackets: α-pinene (1.32 min), chloroform (0.92 min), hexadecane (3.3 min) and dichlorocyclopropane product (3.66 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. In order to isolate the product from the cold reaction mixture, 50 ml of ether was added to it, the ether layer was decanted using a separating funnel, and the compound was further purified using silica gel column chromatography using benzene and ethyl acetate (20:80, v/v) as solvent.

FT-IR (KBr), cm^{-1}: 719 (C–Cl); ^1H NMR (200 MHz, $CDCl_3$) δ: 1.12 (s, 6H, CH_3), 1.22 (s, 3H, CH_3), 1.33–1.38 (m, 4H, CH_2), 1.39–1.42 (m, 2H, CH), 2.25 (t, 1H, J = 5.0 Hz, CH).

3. Results and discussion

3.1. Characterization of TTEAMCM

Initially, mesitylene was chloromethylated using paraformaldehyde and conc. HCl and structure of the product **II** was confirmed from the appearance of C–Cl stretching frequency at 723 cm^{-1} in FT-IR spectrum. Further, the compound **II** was converted into TTEAMCM **III** by quaternization reaction with triethylamine. The formation of TTEAMCM was confirmed from the disappearance of C–Cl stretching frequency at 723 cm^{-1} and appearance of C–N stretching frequency at 1093 cm^{-1} in FT-IR. Similarly, in ^1H NMR analysis, the quaternized ethyl group containing methyl and methylene proton appeared as triplet and quartet at 1.26 ppm and at 3.31 ppm respectively. Further, in ^{13}C NMR, the presence of *N*-ethyl group containing methyl and methylene carbon noticed as a high intense peak at 7.3 and 57.2 respectively.

3.2. Kinetic study

The catalytic behavior of the new MPTC, viz., TTEAMCM was examined through dichlorocarbene addition to α-pinene reaction using 20% (w/w) aqueous NaOH and chloroform in excess under pseudo-first order conditions. The obtained product was isolated and characterized by spectral analyses. The kinetic study for dichlorocarbene addition to α-pinene was conducted by varying the experimental parameters such as stirring speed, [substrate], [catalyst], [NaOH] and temperature and the results are discussed.

3.2.1. Effect of stirring speed

The effect of varying the stirring speed on the rate of dichlorocarbene addition to α-pinene using TTEAMCM was studied in the range of 100–800 rpm. The other parameters, viz., [NaOH], [substrate], [catalyst] and temperature were kept constant. From the plots of $\log(a-x)$ versus time, the pseudo-first order rate constants were evaluated. Initially, the rate is found to increase steadily when the stirring speed was increased from 100 to 400 rpm and a sharp increase in rate was observed at a speed of 500 rpm. Further increase in stirring speed does not alter the reaction rate (Fig. 1). From the observed results, it is clear that the reaction kinetics is controlled by the chemical reaction in the organic phase for stirring rate greater than 500 rpm. Further at stirring speed of 500 rpm, anion exchange equilibrium is very fast relative to the organic displacement reaction. The rate of the substrate consumption becomes independent of stirring speed. Below 500 rpm, the requirement for sufficient rapid mass transfer of the reaction anion is not met and diffusion controlled kinetics is observed. Hence, the constancy of

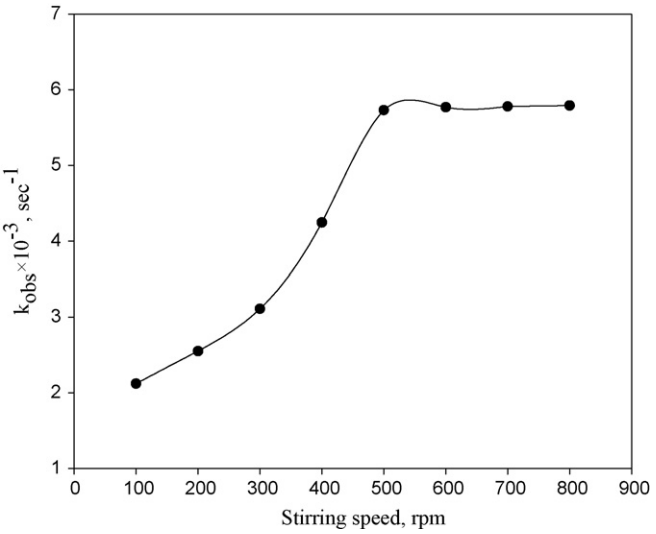


Fig. 1. Effect of variation of stirring speed.

reaction rate constant at above 500 rpm suggested that the reaction might proceed via an interfacial mechanism in the presence of TTEAMCM.

In the two-phase reaction system, the interpretation of the effect of stirring speed on the Stark's extraction mechanism [26] and Makosza's interfacial reaction mechanism [27] are quite different. For an extraction mechanism reaction system, the reaction rate no longer increases with the increase in agitation speed above 300 rpm. However, in the case of interfacial mechanism, the reaction rate increases with the increase in agitation speed even when it is greater than 1000 rpm. The main reason is that the two-phase interfacial mass transfer area, which can influence the reaction rate, also increases with the increase in stirring speed. Balakrishnan and Jayachandran [28] observed a similar trend in dichlorocarbene addition to styrene and C-alkylation of phenyl acetone using ethyl iodide. Chiellini and coworkers [29] reported a continuous increase in the rate of ethylation of phenylacetone even upto stirring speed of 1950 rpm. Similar observation was reported by Wang and Hsieh [9] who studied the kinetics of dichlorocyclopropanation of 4-vinyl-1-cyclohexene and proposed the interfacial mechanism. Recently, Rajendran and Wang [30] also reported the dependence of stirring speed on the rate of reaction upto 700 rpm for dichlorocarbene addition to allyl phenyl ether and proposed an interfacial mechanism. In the present study, the rate of the reaction increases with the increase in the stirring speed up to 500 rpm, which agrees well with the interfacial reaction mechanism rather than Stark's extraction mechanism.

3.2.2. Effect of [substrate]

The effect of varying the concentration of α-pinene on the rate of dichlorocarbene addition to α-pinene was studied in the range of 3.15–15.75 mmol keeping the other parameters as constant. The observed rate constants increase as the amount of substrate increases (Fig. 2). Normally, at high substrate concentration, the availability of the catalyst per mole of substrate to catalyze the reaction is low. But in the present study, though the molar ratio of substrate with respect to catalyst increased due to the presence of more active sites (in the case of MPTC), the reaction rate is increased with increase in substrate concentration. A similar trend was observed by Balakrishnan et al. [31] in the study of C-alkylation of phenylacetone with *n*-bromobutane using benzyltriethylammonium chloride as PTC. Balakrishnan and Jayachandran [28] also reported the same dependency of rate constant on the substrate

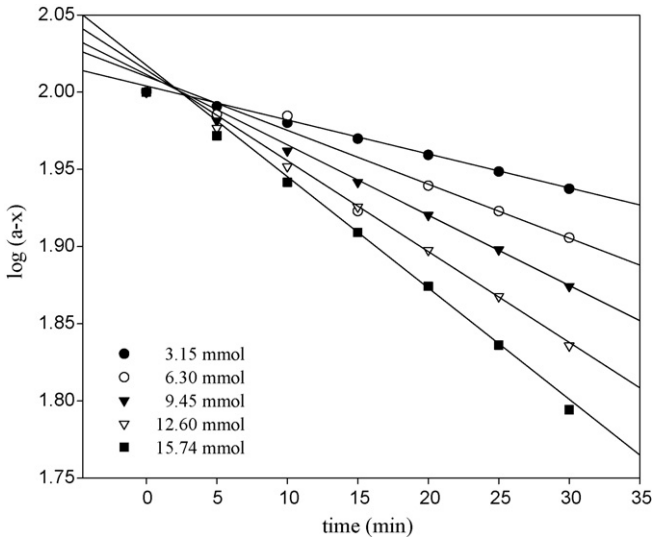


Fig. 2. Effect of variation of substrate concentration.

Table 1
Effect of variation of catalyst amount

[Catalyst] (mmol)	k_{obs} ($\times 10^{-3}$ s^{-1})	5 + log [catalyst]	3 + log k_{obs}
0.18	2.63	0.2553	0.4199
0.26	4.85	0.4224	0.6857
0.35	5.46	0.5474	0.7372
0.44	6.22	0.6443	0.7938
0.53	7.59	0.7235	0.8802

concentration for C-alkylation of phenylacetonitrile. A same trend of observation was also reported for the dichlorocarbene addition to citral using a multi-site PTC [11].

3.2.3. *Effect of [catalyst]*

The catalyst concentration has important effect on the rate of dichlorocarbene addition to α-pinene. The concentration of TTEAMCM was varied from 1.76×10^{-4} to 5.29×10^{-4} mmol. The observed results demonstrated that the rate of reaction is linearly dependent on the amount of catalyst added (Table 1). As seen in the experimental plots (Fig. 3), the reaction rate is increased with

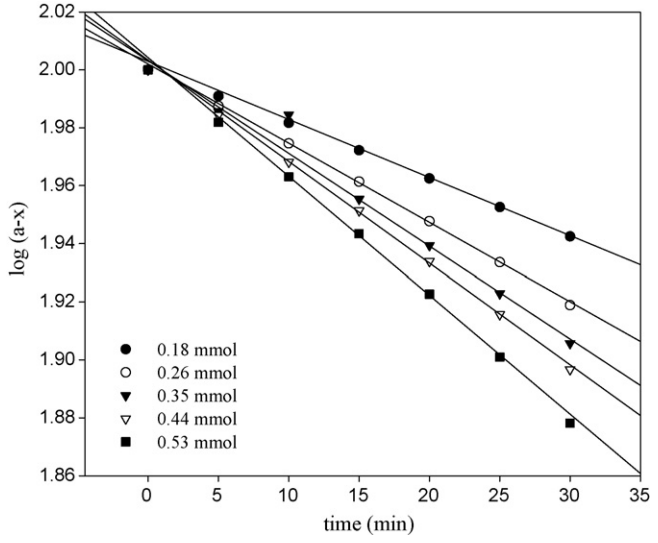


Fig. 3. Effect of varying catalyst amount.

the increase in the amount of catalyst. On increasing the catalyst concentration, the number of active sites in the reaction medium is raised that provide effective collision between Na^+CCl_3 (interface) and the active site $N^+Et_3Cl^-$ (interface). Therefore, the probability of forming a complex between $N^+Et_3Cl^-$ (org) and dichlorocarbene is largely increased, i.e. the concentration of dichlorocarbene in the organic phase is enhanced. Hence, apparently the rate constant is increased with the increase in the amount of catalyst.

Control experiments was also carried out for dichlorocarbene addition to α-pinene in the absence of catalyst under specified conditions in which no product was observed even after 3 h of reaction. Starks reported similar observation in the study of dichlorocarbene addition to cyclohexene using tridecylmethylammonium chloride as a PTC [32]. In the study of the dehydrobromination of phenethyl bromide in the presence of tetraoctylammonium bromide [33], a zero order kinetics with respect to catalyst was observed. The effect of catalyst structure is very important, especially in dichlorocarbene addition reactions which was explained by Dehmlow's comparative study [21] in the dichlorocarbene addition to cyclohexene using different catalysts with high yields of products. Wang and coworker [34] reported the same observation in the dichlorocyclopropanation of dicyclopentadiene by employing aqueous NaOH and chloroform in excess in the presence MPTC.

3.2.4. *Effect of [NaOH]*

The dichlorocarbene addition is mainly dependent on the concentration of alkali. Dichlorocarbene ($:CCl_2$) is being generated from chloroform in the presence of alkaline solution and subsequently it reacts with organic-phase reactant (i.e. α-pinene) to produce the desired product. Therefore, the rate of dichlorocarbene addition is highly influenced by the concentration of alkali in aqueous solution. Kinetic experiments were carried out by employing 2.78–7.06 M NaOH. The observed experimental results (Table 2) indicate that the reaction rate is slow at low alkaline concentration. However, the reaction is dramatically enhanced when the concentration of alkali is increased (Fig. 4). The main reason is that the hydration of OH^- is minimized and the activity of OH^- is increased by increasing the concentration of alkali. Further, under this condition, the hydrolysis of dichlorocarbene is also minimized which in turn facilitating the reaction to proceed. A similar trend was observed by Balakrishnan and Jayachandran [28] in using TEBAC to initiate the dichlorocyclopropanation of styrene.

This phenomenon is well explained by the interfacial mechanism, i.e. the reaction of chloroform, quaternary ammonium salt and sodium hydroxide on the interface between organic and aqueous phases. On increasing the concentration of alkali, the rate of ion-exchange occurs on the interface would be accelerated. Meanwhile, the inorganic salt produced from the interfacial region then transfers to the aqueous phase, so it is favorable for the reaction being carried out and generating intermediate species. In a systematic kinetic study of dichlorocarbene addition to styrene using TEBAC as a catalyst, 50% NaOH was employed, whereas in the present study 20% NaOH is the optimum concentration required to get higher conversions. A lower amount of NaOH is of specific interest in industry as there is a scope of easy reaction work up

Table 2
Effect of variation of [NaOH]

[NaOH] (M)	k_{obs} ($\times 10^{-3}$ s^{-1})	Log [NaOH]	4 + log k_{obs}
2.78	3.77	0.4440	0.5760
3.74	4.71	0.5729	0.6429
4.41	5.40	0.6444	0.7025
5.86	5.77	0.7679	0.7610
7.06	6.12	0.8488	0.7856

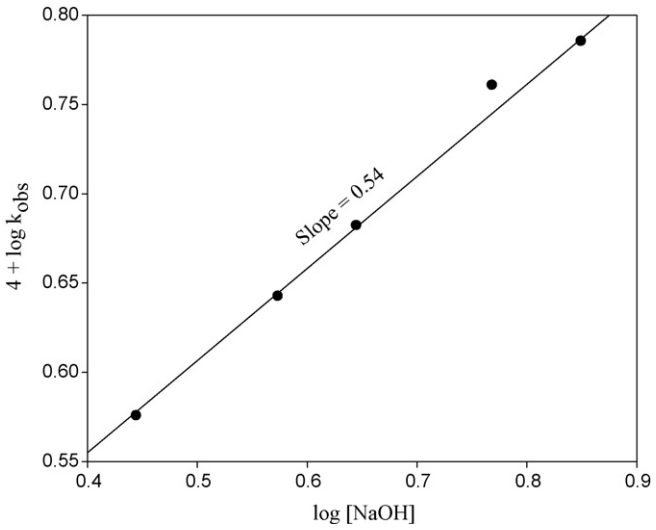


Fig. 4. Effect of [NaOH] on k_{obs}.

and durability of the reaction vessels. Similar dependence on NaOH concentration was also observed by Wang et al. [9,30] and Jayachandran and Wang [34] in dichlorocyclopropanation reactions.

3.2.5. Effect of temperature

The influence of varying temperature on the rate of reaction of α-pinene with chloroform was carried out in the temperature range from 303 to 323 K. The kinetic profile of the reaction is obtained by plotting $\log(a-x)$ versus time. The reaction rate constant increases with the increase in temperature. The energy of activation is calculated from Arrhenius plot (Fig. 5), E_a = 15.3 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 α-pinene were found to be −23.1 cal K^{-1} mol^{-1}, 14.7 and 22.5 kcal mol^{-1} respectively.

In the early studies, the activation energy for the ethylation of pyrrolidin-2-one under PTC condition was reported to be 12.4 kcal mol^{-1} and for this an interfacial mechanism was proposed [35]. Similarly, E_a value for ethylation of phenylacetonitrile was reported to be 20 kcal mol^{-1} suggesting an interfacial mechanism [29]. In a comprehensive study on the dichlorocarbene addition to isobutylene, it has been observed that the formation of 1,1-dichloro-2,2-dimethylcyclopropane increases with increase in temperature and the E_a value was found to be 12.3 kcal mol^{-1}. Do and Chou [36] observed a favorable effect on the extraction of tetrabutylammonium hypochlorite ion-pair from the aqueous phase into the organic phase on increasing the temperature in the study of the oxidation of benzyl alcohol by hypochlorite ion under PTC conditions. A higher E_a value has been reported [33] for the polystyrene bound triethylammonium ion catalyzed reaction, which was controlled by strict intrinsic reactivity under triphase reactions. The E_a value for the dichlorocyclopropanation of 1,7-octadiene was reported to be 13.42 kcal mol^{-1} and for this an interfacial mechanism has been proposed [37]. Taking into consideration of earlier studies and their observations, in our study also a higher E_a value, i.e. 15.3 kcal mol^{-1} was observed for dichlorocarbene addition to α-pinene and hence the reaction should proceed through an interfacial mechanism.

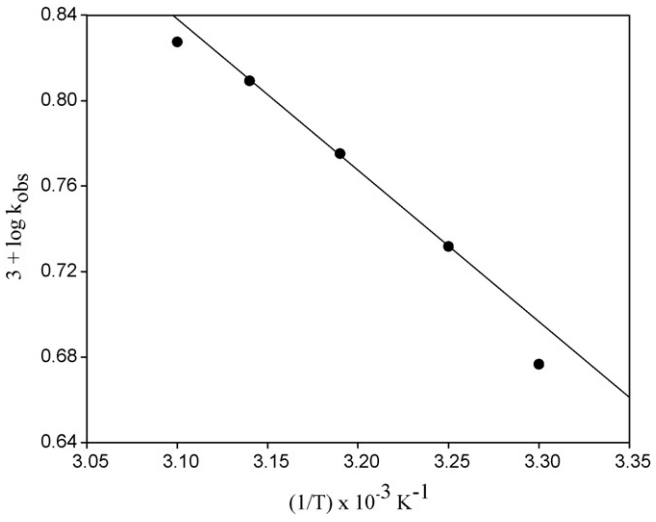


Fig. 5. Arrhenius plot: effect of temperature.

3.3. Comparison of rate constant using different phase transfer catalysts

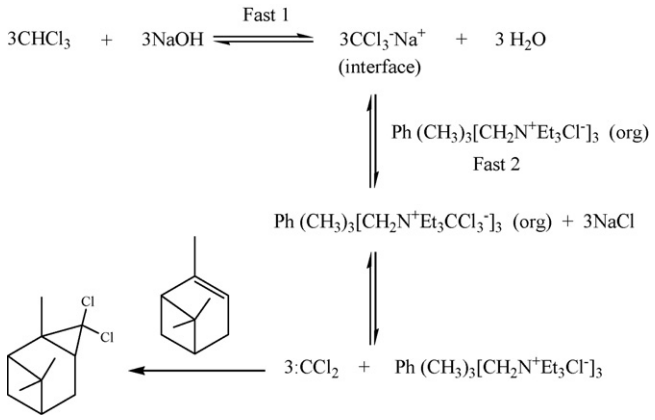
The relative catalytic efficiency of new tri-site PTC (TTEAMCM) was determined by conducting the dichlorocarbene addition to α-pinene reaction using various commercial single-site PTCs, viz., tetraethylammonium chloride (TEAC), tetraethylammonium bromide (TEAB), benzyltriethylammonium bromide (TEBAB) and benzyltriethylammonium chloride (TEBAC) under identical experimental conditions. From the observed results (Table 3), it was found that TTEAMCM was ca. three times more active than the commercial single-site PTCs as evidenced by a threefold enhancement in rate constant. That is, the rate of the reaction is directly proportional to the number of active sites present in the catalyst. This observation proves that in TTEAMCM must contain three active sites and all these catalytic sites had co-operatively involved in the dichlorocarbene addition reaction.

3.4. Mechanism (Scheme 3)

Dichlorocarbene addition reaction may occur in two steps. Initially, base deprotonation of chloroform catalyzed by a phase transfer agent occurs and followed by addition of electrophile taking place. The selectivities of dichlorocarbene generated under MPTC conditions towards the alkenes are independent of the structure of the catalysts. This means that the species: CCl_2 is involved in all cases whereas there is a strong influence of the reaction medium starting from trihalocarbene to dihalocarbene [17]. In the phase transfer system, two major mechanisms are believed to be operative, viz., Stark's extraction mechanism [26] characterized by increased reaction rate with increased organophilicity, independence of reaction rate on stirring speed above certain value and linear dependence of reaction rate on catalyst concentration and Makosza's interfacial mechanism [27] characterized by maximum reactivity with relatively hydrophilic quaternary salts. Usually alkyltriethylam-

Table 3
Comparison of rate constant k_{obs} using different single-site PTCs

Entry	Catalysts	[Catalyst] (×10^{-4} mmol)	k_{obs} (×10^{-3} s^{-1})
1	Control	–	Nil
2	TEAC	3.5	1.45
3	TEAB	3.5	1.29
4	TEBAC	3.5	1.91
5	TEBAB	3.5	1.64
6	TTEAMCM	3.5	5.47



Scheme 3. Interfacial mechanism for dichlorocarbene addition to α-pinene.

monium halides increased reaction rate with increased speed even up to 1950 rpm and fractional order with respect to catalyst.

From the observed experimental results, the dependence of kinetic data on the stirring speed up to 500 rpm, concentrations of the catalyst, aqueous hydroxide ions, temperature and higher E_a value strongly prove that this reaction proceeded via the 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. Then the MPTC catalyst anion was exchanged by haloderivative to form an active intermediate of MPTC/CCl_3^- which can react with the olefinic group containing α-pinene to give an mono-dihalocyclopropanated product. Furthermore, the concentration of catalytic site per molecule is increased from single-site to multi-site (tri-site) as a result of that the abstraction of proton from chloroform is more effective than the single-site PTC.

4. Conclusion

We have successfully prepared a novel soluble multi-site (tri-site) phase transfer catalyst, viz., 2,4,6-tris (triethylammonium-methylene chloride) mesitylene (TTEAMCM) from mesitylene using a simple two-step procedure. The presence of tri-active sites in TTEAMCM catalyst was confirmed by FT-IR, ^{1}H NMR, ^{13}C NMR and chloride ion analyses. Further, the approximate threefold enhancement in pseudo-first order rate constant for TTEAMCM catalyst when compared with commercial single-site PTCs in catalyzing the dichlorocarbene addition to α-pinene reaction has also proved that the new catalyst contains three active sites in a molecule.

Further, for the first time, detailed kinetic study was conducted for dichlorocarbene addition to α-pinene using TTEAMCM. The observed rate constants are found to be dependent of the each kinetic variable such as stirring speed, [substrate], [catalyst], [NaOH] and temperature. Furthermore, the activation energy E_a and the thermodynamic parameters such as $\Delta S^{\#}$ $\Delta H^{\#}$ and $\Delta G^{\#}$ values were also evaluated for the first time and reported. Based on the kinetic and thermodynamic parameters, we propose an interfacial mechanism for the dichlorocarbene addition to α-pinene.

Acknowledgements

The financial support from the University Grants Commission (UGC), New Delhi, India, is gratefully acknowledged and one of the authors P.G. thanks Council of Scientific and Industrial Research (CSIR), New Delhi, India, for providing the financial assistance (SRF).

References

[1] J.C.R. Jarrouse, Hebd. Seances Acad. Sci. Ser. C 232 (1951) 1424.
[2] H.H. Freedman, Pure Appl. Chem. 58 (6) (1986) 857.
[3] C.M. Starks, C.L. Liotta, Phase Transfer Catalysis, Academic Press, New York, 1978 (Chapter 2).
[4] E.V. Dehmlow, S.S. Dehmlow, Phase Transfer Catalysis, Verlag, Weinheim, 1993.
[5] C.M. Starks, C.L. Liotta, M. Halpern, Phase Transfer Catalysis: Fundamentals, Applications and Industrial Perspectives, Chapman, New York, 1994.
[6] M. Halpern, Phase Transfer Catalysis Communications 3 (1997) 33.
[7] J.P. Idoux, R. Wysocki, S. Young, J. Turcot, C. Ohlman, R. Leonard, Synth. Commun. 13 (1983) 139.
[8] T. Balakrishnan, W.T. Ford, Tetrahedron Lett. 22 (1981) 4377.
[9] M.L. Wang, Y.M. Hsieh, J. Mol. Catal. A: Chem. 210 (2004) 59.
[10] T. Balakrishnan, E. Murugan, A. Siva, Appl. Catal. A: Gen. 273 (2004) 89.
[11] E. Murugan, A. Siva, J. Mol. Catal. A: Chem. 235 (2005) 220.
[12] A. Siva, E. Murugan, J. Mol. Catal. A: Chem. 241 (2005) 101.
[13] E. Murugan, A. Siva, Synthesis (2005) 2022.
[14] A. Siva, E. Murugan, J. Mol. Catal. A: Chem. 241 (2005) 111.
[15] A. Siva, E. Murugan, Synthesis (2005) 2927.
[16] A. Siva, E. Murugan, J. Mol. Catal. A: Chem. 248 (2006) 1.
[17] W. Kirmse, Carbene Chemistry, Academic Press, New York/London, 1971.
[18] M. Makosza, M. Wawrzyniewicz, Tetrahedron Lett. 10 (1969) 4659.
[19] W.E. Doering, A.K. Hoffmann, J. Am. Chem. Soc. 76 (1954) 6162.
[20] E. Dunkelblum, B. Singer, Synthesis (1975) 323.
[21] E.V. Dehmlow, Tetrahedron Lett. 17 (1976) 91.
[22] A.N. Vereshchagin, S.G. Vulfson, N.I. Gubkina, B.A. Arbuzov, Seriya Khimicheskaya 11 (1970) 2467.
[23] S. Julia, A. Ginebreda, Synthesis (1977) 682.
[24] T. Balakrishnan, E. Murugan, J. Polym. Sci. A: Polym. Chem. 42 (2003) 347.
[25] H.J. Choi, Y.S. Park, H.S. Kim, C.S. Cho, K. Ko, K.H. Ahn, Org. Lett. 4 (2002) 795.
[26] C.M. Starks, R.M. Owens, J. Am. Chem. Soc. 95 (1973) 3613.
[27] M. Makosza, E. Bialecka, Tetrahedron Lett. 18 (1977) 183.
[28] T. Balakrishnan, J.P. Jayachandran, J. Chem. Soc., Perkin Trans. 2 (1995) 2081.
[29] R. Solaro, S. D'Antone, E. Chiellini, J. Org. Chem. 45 (1980) 4179.
[30] V. Rajendran, M.L. Wang, J. Mol. Catal. A: Chem. 288 (2008) 23.
[31] T. Balakrishnan, K. Arivalagan, R. Vadukut, Ind. J. Chem. B 34 (1992) 338.
[32] C.M. Starks, J. Am. Chem. Soc. 103 (1981) 3821.
[33] M. Tomoi, W.T. Ford, J. Am. Chem. Soc. 103 (1981) 3821.
[34] J.P. Jayachandran, M.L. Wang, Appl. Catal. A: Gen. 206 (2001) 19.
[35] W.P. Reeves, R.G. Hilbrich, Tetrahedron 32 (1976) 2235.
[36] J.S. Do, T.C. Chou, Ind. Eng. Chem. Res. 29 (1990) 1095.
[37] M.L. Wang, Y.M. Hsieh, R.Y. Chang, J. Mol. Catal. A: Chem. 198 (2003) 111.