



Triphase catalytic activity of a new insoluble multi-site phase transfer catalyst in C-alkylation of dihydrocarvone—A kinetic study

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 18 December 2008
Received in revised form 21 March 2009
Accepted 18 April 2009
Available online 3 May 2009

Keywords:

Triphase catalysis
C-alkylation
Dihydrocarvone
Interfacial mechanism

ABSTRACT

A new insoluble multi-site triphase catalyst viz., polymer-supported 1,3,4-tris(triethylammonium-methylene chloride)-2-methylbenzene (PSTTACMB) containing three active sites was synthesized by simplified procedure and its structure was characterized by FT-IR, solid ^{13}C NMR, TGA, [chloride ion] and SEM analyses. The catalytic efficiency of PSTTACMB was ascertained by comparing with insoluble single-site PTC viz., polymer-supported benzyltriethylammonium chloride (PSBTEAC) through determination of pseudo-first order rate constant for C-alkylation of dihydrocarvone with 1-bromobutane using 25% (w/w) NaOH at 60 °C under identical experimental conditions. Further, the dependency of rate of C-alkylation of dihydrocarvone on different kinetic variables was studied by varying the stirring speed, [substrate], [catalyst], [NaOH] and temperature. Based on the observed kinetic results and activation energy, a suitable mechanism was proposed.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Phase transfer catalysis has been emerged as an important synthetic tool in organic chemistry to carry out the reactions between a water-soluble reactant and a water-insoluble reactant present in biphasic medium [1–3]. The enhanced reaction rate, improved selectivities and high yield under very mild conditions are the main advantages of phase transfer catalyst (PTC) which makes it attractive as a challenging technique for industrial preparation of fine chemicals and pharmaceuticals [4,5]. Most of the industrial PTC reactions are carried out almost exclusively with homogeneous soluble PTCs. However, the main problem in using soluble PTC is their recovery i.e. the separation of the catalyst from the product is difficult and that may significantly affect the cost and purity of the product. To overcome this problem, “Triphase Catalysis” a new type of heterogeneous catalysis introduced by Regen [6] in which the catalyst was immobilized on an insoluble polymeric matrix i.e. polymer-supported PTC (PS-PTC). These triphase catalysts can be readily separated from the products by simple filtration and be regenerated to their original activity. They can be reused until they lose their mechanical stability and thus be used in continuous reactors and flow systems such as packed and fluidized bed reactors [7–9]. The copolymer of poly(styrene) cross-linked with 2% divinylbenzene is the most common known support used, which may be too gelatinous in swelling solvents for use in many large-scale flow

systems and filtrations. The major drawback of triphase catalysts is that their activity is often less than that of soluble PTCs due to external and intraparticle mass transfer limitations. But there are few reports available in literature in which the polymer-supported PTCs have been shown to have higher reactivity than soluble PTCs [10–13]. However, the industrial utilities of both of these soluble and insoluble PTCs containing single active site are limited due to their low activity in the reaction. It is also found that relatively large amount of single-site PTC must be required to perform the bench-mark scale reaction and also to proceed rapidly enough to form the products in an economically feasible time period. Further, the choice of PTC mainly depends on magnitude of economy, higher efficiency and low energy requirements. Therefore, this conventional soluble/insoluble single-site PTCs have not fulfilled these requirements. As a result, the multi-site PTCs (MPTCs) containing more than one active site have been developed as an alternative and which can be used in smaller proportions to get enhanced reactivity.

Idoux et al. [14] was the first who reported the multi-site phosphonium PTC containing three active sites as soluble and insoluble polymer-supported catalysts and their catalytic activity in simple SN_2 and some weak nucleophile–electrophile SN_Ar reactions were studied. Subsequently, soluble ammonium type PTCs containing two and three active sites have been synthesized by Balakrishnan and Jayachandran [15] and applied for various alkylations and carbene addition reactions. Benaglia et al. [16] had reported the synthesis of PEG-supported ammonium tetra-site PTC and found that an increase in the number and a proper spatial arrangement of the catalytic sites thus providing more efficient catalyst. Wang et al.

* Corresponding author. Tel.: +91 44 22202818/22202819; fax: +91 44 22352494.
E-mail address: murugan.e68@yahoo.com (E. Murugan).

synthesized various MPTCs and their catalytic activity was studied using thioether synthesis, dichlorocyclopropanation and alkylation reactions [17–20]. The total weight of MPTC required in these reactions is largely less compared to related single-site PTCs and also no doubt that the number of catalytic site can ultimately decide the efficiency of reaction. Thus reflecting to control the economy of the reaction process. In our laboratory, we also reported different soluble MPTCs for alkylation reactions [21,22], dichlorocarbene addition [23,24] and asymmetric synthesis [25–28] and insoluble bead-shaped polymer-supported tri-site and six-site PTC for N-alkylation of pyrrole [29] and Darzen's condensation [30] respectively. Recently, Srivastava and Srivastava [31] reported insoluble calix[4]arene based multi-site PTCs and their catalytic activity has been investigated through Darzens condensation, O/N-alkylation and ethylbenzene oxidation reactions.

C-alkylation of ketones is one of the most widely studied PTC reactions in fine chemical industries which provide pharmaceutically valuable products or intermediates for the synthesis of perfumes, fragrances and plant protection agents [32]. In the recent past, alkylation of terpenoids was immensely popular owing to its pharmaceutical applications [33–35]. Dihydrocarvone is one of the important terpenes and its alkylated products are used in aroma industries [36]. Further, there are no reports available on the C-alkylation of dihydrocarvone using PS-MPTC. In view of the above-mentioned discussions, in the present study, we have synthesized a novel polymer-supported multi-site PTC containing three active sites and its catalytic efficiency was studied through C-alkylation of dihydrocarvone with 1-bromobutane.

2. Experimental

2.1. Chemicals

Gelatin (Lancaster), boric acid (SRL), polyvinyl alcohol (Lancaster), styrene (Lancaster), divinylbenzene (Lancaster), vinylbenzylchloride (Lancaster), AIBN (Lancaster), triethylamine (Merck), triethyl methanetricarboxylate (Lancaster), lithium aluminium hydride (Merck), phosphorus trichloride (Lancaster), dihydrocarvone (alfa aesar), 1-bromobutane (SRL), sodium hydroxide (SRL), potassium carbonate (Merck), dimethyl formamide (SRL), tetrahydrofuran (SRL), dichloromethane, acetonitrile (SRL), methanol (SRL), acetone (SRL), diethylether (SRL) were used as provided.

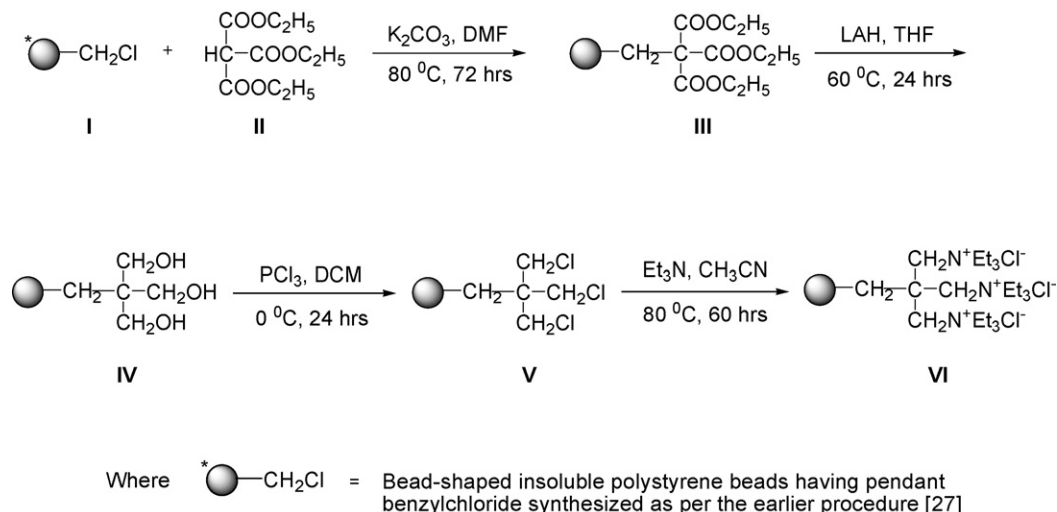
2.2. Instrumentation

The FT-IR spectra were recorded on Bruker-Tensor 27 FT-IR spectrophotometer. Solid ^{13}C NMR spectrum was recorded using AMX-400 MHz spectrometer and thermogravimetric analyses (TGA) were carried out in a ZETZSCH-STA 409C thermal analyzer. The surface-morphology study was performed using JEOL JSM-6360 scanning electron microscope (SEM). The kinetic study for C-alkylation of dihydrocarvone was performed by monitoring the disappearance of dihydrocarvone quantitatively through gas chromatograph (Varion-3700 interfaced with a Chromatograph I/F module) analysis using flame ionization detector. The column used for the product analysis was 5% SE-30, chrom WHP 80/100, $3 \text{ m} \times 1/8 \text{ in.}$ stainless tube.

2.3. Synthesis of insoluble bead-shaped multi-site PTC (tri-site) viz., polymer-supported 1,3,4-tris(triethylammoniummethylene chloride)-2-methylbenzene (PSTTACMB) (Scheme 1)

The insoluble polymer-supported beads were prepared by following the procedure described in the early literature [37] i.e. by conducting the polymerization reaction using vinylbenzylchloride (25%, 0.27 mol) as a functional monomer, divinylbenzene (2%, 0.04 mol) as a cross-linking monomer and styrene (73%, 1.13 mol) as a supporting monomer via suspension polymerization technique. The obtained cross-linked copolymer beads **I** were washed with methanol repeatedly and then dried. Then the dried copolymer beads were sieved into different mesh size using Testing Sieve Shaker (RO-TAP, W.S. Tyler Company, Ohio). From the sieved beads, 2 g (+120–140 mesh size) were swelled in DMF (30 ml) for about 24 h in a 150 ml RB flask. To which 20 ml of triethyl methanetricarboxylate and K_2CO_3 (2 g) were added to the swelled beads and the reaction mixture was stirred continuously for 72 h at 80°C . The resulting condensed form of polymer beads **II** were filtered, washed with methanol (20 ml) followed by water (40 ml) and dried at 60°C for 18 h. The condensed polymer beads **II** were swelled in dry THF (20 ml) for 12 h. Then 0.5 g of LiAlH_4 was added and the mixture was refluxed for 24 h, as a result, the ester groups were reduced into primary alcoholic groups. After completion of reaction, 15 ml of methanol was added and the resulting condensed polymer beads **III** was filtered and washed with acetone ($2 \times 30 \text{ ml}$) and dried for 18 h at 60°C .

The polymer-bound product **III** containing ester groups was swelled in 30 ml of dichloromethane for overnight and then 15 ml of



Scheme 1. Synthesis of insoluble bead-shaped tri-site PTC viz., polymer-supported 1,3,4-tris(triethylammoniummethylene chloride)-2-methylbenzene (PSTTACMB).

phosphorus trichloride (PCl_3) was added slowly (dropwise) at 0°C . After the addition, the reaction mixture was stirred at room temperature for 24 h, as a result, the hydroxyl groups of $-\text{CH}_2\text{OH}$ present in **III** were converted into $-\text{CH}_2\text{Cl}$. The obtained chlorinated beads **IV** were filtered and washed with diethylether (25 ml) and acetone (25 ml). Finally, the chlorinated beads **IV** were allowed to swell in acetonitrile (50 ml) for overnight and the swelled beads were quaternized by stirring with excess of triethylamine (40 ml) for about 60 h at 80°C in an inert atmosphere (N_2). The solvent and unreacted triethylamine present in the resulting mixture was removed by filtration and washed with acetonitrile (2×25 ml), methanol (3×25 ml) and acetone (3×25 ml) and then dried in an oven at 60°C for about 12 h and thus produced the insoluble tri-site PTC viz., polymer-supported 1,3,4-tris(triethylammoniummethylene chloride)-2-methylbenzene PSTTACMB **V**.

Yield—82%.

$[\text{Cl}^-]$: 2.79 mequiv. g^{-1} (Volhard's method)

FT-IR: 2931 (aliphatic C–H), 1173 (C–N)

2.4. Preparation of sample for FT-IR and SEM analyses

FT-IR study was conducted (arbitrary or semi-quantitative) to determine the number of active sites available in both catalysts i.e. tri-site PSTTACMB and single-site PSBTEAC by taking equal amount of the respective catalyst along with KBr (1:1 ratio); the pellet was carefully prepared by using the total weight of each sample with uniform thickness. The uniformity of the thickness of the respective pellet was maintained through dial micrometer. Similarly, the surface morphology of the bead-shaped tri-site PS-MPTC viz., PSTTACMB and reported single-site PSBTEAC having mesh size of +120–140 were analyzed through SEM. The non-conductive polymeric materials are made into conductive by giving uniform platinum coating. The respective catalyst samples were spread on the surface of double sided adhesive tape, one side of which was already adhered to surface of a circular copper disc pivoted by a rod. JEOL JSM-6360 auto-fine-coating ion sputter was used for the platinum coating under identical experimental conditions.

2.5. 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 experiments for C-alkylation of dihydrocarvone (Scheme 2) catalyzed by PSTTACMB and single-site PSBTEAC in the presence of aqueous sodium hydroxide were carried out by the reverse addition method i.e. delayed addition of alkylating agent viz., 1-bromobutane. The substrate dihydrocarvone (6.1 mmol), aqueous NaOH 25% (w/w) (25 ml), hexadecane (1 ml) and the respective catalysts single/tri-site containing 0.74 mequiv. of $[\text{Cl}^-]$ were taken individually in the RB flask and then stirred at 500 rpm for 5 min at 60°C so as to stabilize the catalyst and substrate. Then the stirring speed was increased to 600 rpm and 20 ml of 1-bromobutane (alkylating agent) was added to the reaction mixture at zero time. Samples were collected from the organic layer of the mixture by stopping the stirring for 10–15 s in each time at regular intervals (every 5 min). The kinetics of the reaction

was followed by estimating the disappearance of dihydrocarvone using gas chromatograph. The column (5% SE-30 chrom WHIP 80/100, $3\text{ m} \times 1/8$ in. stainless steel packed column) was maintained at 200°C . For every sample, $0.5\ \mu\text{l}$ of reaction mixture was injected to the column and the products were analyzed; the retention times for each reactants/product were mentioned within the parenthesis: dihydrocarvone (1.17 min), 1-bromobutane (0.70 min), mono and dialkylated products (2.79 and 1.93 min, respectively). The pseudo-first order rate constants were calculated from the plots of $\log(a-x)$ versus time.

3. Results and discussion

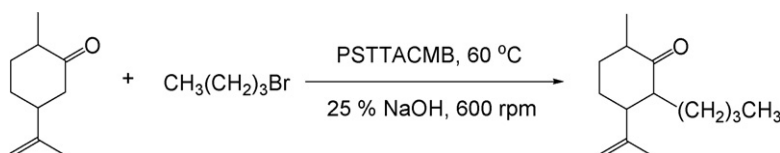
3.1. Characterization of PSTTACMB

3.1.1. FT-IR and ^{13}C NMR analyses

Initially, the styrene based cross-linked polymer-supported beads **I** were prepared by following the existing procedure [37] and then reacted with triethyl methanetricarboxylate **II** and K_2CO_3 in DMF medium which in turn gives product **III**. The appearance of characteristic C=O stretching (ester) at $1735\ \text{cm}^{-1}$ in FT-IR spectrum (Fig. 1b) confirms the formation of product **III**. The ester groups present in product **III** were allowed for reduction using LiAlH_4 and converted into alcohol groups to yield **IV**. The availability of O–H stretching noticed at $3408\ \text{cm}^{-1}$ in FT-IR spectrum (Fig. 1c) had confirmed the reduction of ester groups into alcohol. Further, CH_2OH groups present in the product **IV** were chlorinated using PCl_3 ; the resulting chlorinated product **V** was analyzed with FT-IR analysis (Fig. 1d), in which a sharp peak was observed at $714\ \text{cm}^{-1}$ and this must be attributed to the C–Cl stretching and thus confirmed the formation of product **V**. Finally, the chlorinated beads **V** were quaternized using triethylamine and thus produced the tri-site catalyst viz., PSTTACMB **VI**. The availability of active site (or) quaternization reaction was established from the appearance of sharp peak at $1173\ \text{cm}^{-1}$ for C–N stretching in FT-IR spectrum (Fig. 1e). A comparative quantitative FT-IR study was carried out arbitrarily using both the tri-site PSTTACMB **VI** and single-site PSBTEAC (obtained by direct quaternization of styrene based cross-linked polymer-supported beads **I**). From the FT-IR results, the C–N peak intensity of PSTTACMB noticed at $1173\ \text{cm}^{-1}$ (Fig. 1e) was found to be higher/broader than the peak intensity of single-site PSBTEAC (Fig. 1a). In contrast, the C–Cl stretching noticed at $714\ \text{cm}^{-1}$ shows quite opposite observation to that of C–N peak intensity in the respective catalyst. This trend of result in turn reveals that the PSTTACMB catalyst should contain more than one active site than PSBTEAC. Similarly in the ^{13}C NMR spectra of newly synthesized tri-site PSTTACMB (Fig. 2), the peaks observed at 10.4 and 42.3 ppm are pertinent to methyl and methylene carbons present in the quaternized ethyl groups and thus proves the formation of tri-sites in the catalyst.

3.1.2. TGA and chloride ion analyses

Although the availability of tri-site in PSTTACMB was established through the peak intensity of C–N stretching in FT-IR spectrum, the extent of quaternization or presence of multi-active sites in PSTTACMB catalyst was further established by determining the amount of functional group i.e. triethylamine group $-\text{N}(\text{C}_2\text{H}_5)_3$ present in



Scheme 2. C-alkylation of dihydrocarvone using PSTTACMB.

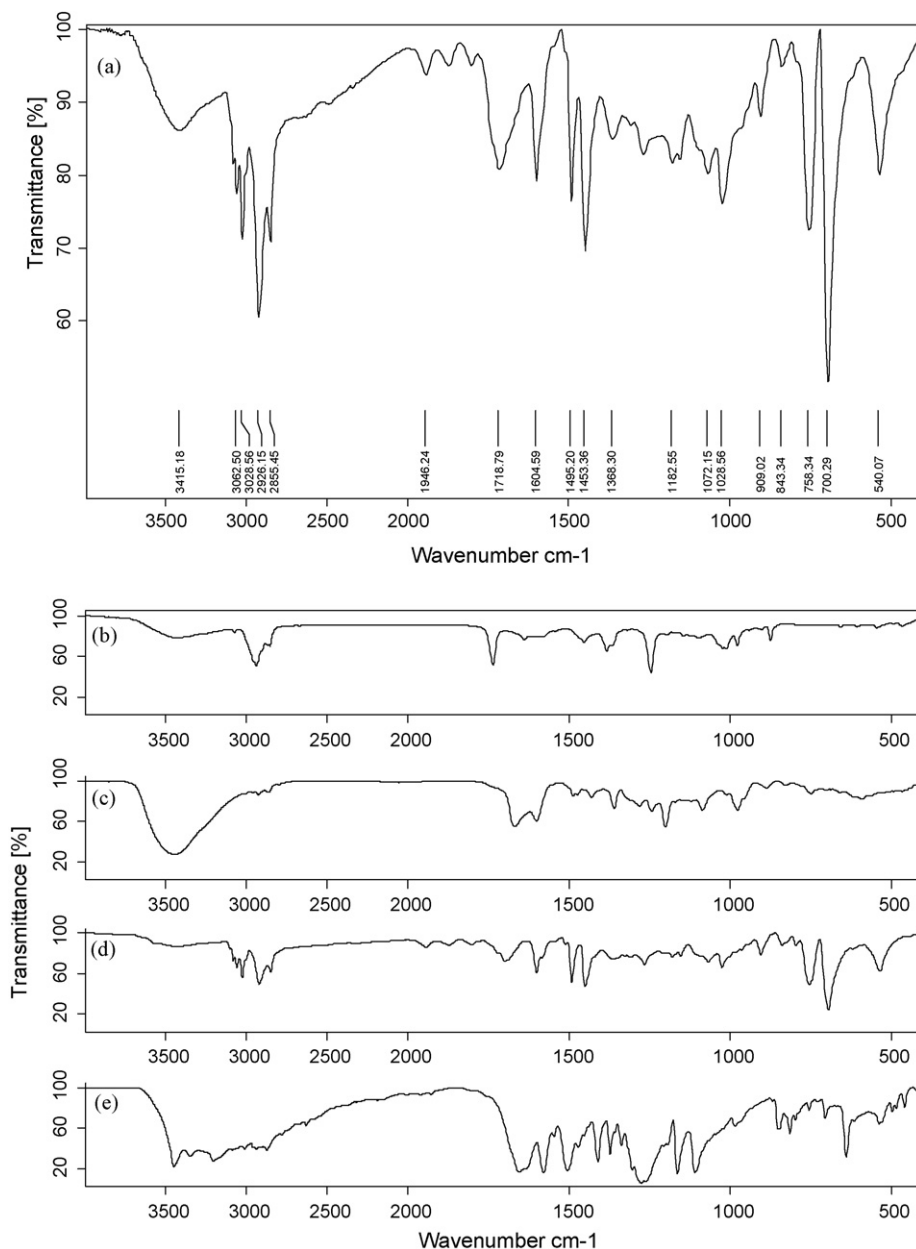


Fig. 1. FT-IR spectrum of (a) single-site PSBTEAC, (b) polymer-supported beads after condensation, (c) polymer-supported beads after reduction, (d) polymer-supported beads after chlorination, and (e) polymer-supported tri-site PSTTACMB.

the catalyst through thermogravimetric analysis (TGA) and it was compared with the single-site PSBTEAC. Wu and Lee [38] reported that the availability of triethylamine groups was normally ascertained from the decomposition temperature at 160 to 200 °C. That is, the amount of functional group $[-N(C_2H_5)_3]$ present in the catalyst was quantitatively determined by measuring the weight loss occurred at 160 to 200 °C. Thus, the weight loss of $-N(C_2H_5)_3$ groups is the direct quantitative indication for the availability of number of active sites present in the respective catalyst. In the present study, for easy understanding, the comparative amount of active sites $[Cl^-]$ determined from the observed weight loss values of $N(C_2H_5)_3$ groups in TGA for single-site PSBTEAC (Fig. 3a) and tri-site PSTTACMB (Fig. 3b) is given in Table 1. The amount of $[Cl^-]$ available in tri-site PSTTACMB catalyst was found to be more (2.88 mequiv. g^{-1}) than single-site PSBTEAC (1.24 mequiv. g^{-1}) which in turn confirms the presence of more than one active site in new PSTTACMB catalyst. Further, the concentration of chloride ion $[Cl^-]$ present in both PST-

TACMB and PSBTEAC catalysts was also estimated through known Volhard's method and found to be 2.79 and 1.12 mequiv. g^{-1} respectively (Table 1). The higher $[Cl^-]$ observed in PSTTACMB catalyst also indicates that it contains more than one active site.

3.1.3. Surface-morphology study of PSTTACMB and PSBTEAC using scanning electron microscope (SEM)

SEM analysis was carried out using tri-site PSTTACMB and single-site PSBTEAC catalysts individually using representative mesh size of +120 – 140. The magnified views of single-bead for both the catalysts were shown in Fig. 4a and b. This comparative microgram results reveal that the surface of single-site PSBTEAC (Fig. 4a) shows a smooth homogeneous surface without tiny nodules. Whereas, in the case of tri-site PSTTACMB, more number of tiny nodules were noticed on the surface of the beads and thus exhibits a heterogeneous surface (Fig. 4b). This kind of observation proves the availability of more number of active sites ($-N^+Et_3Cl^-$) in the

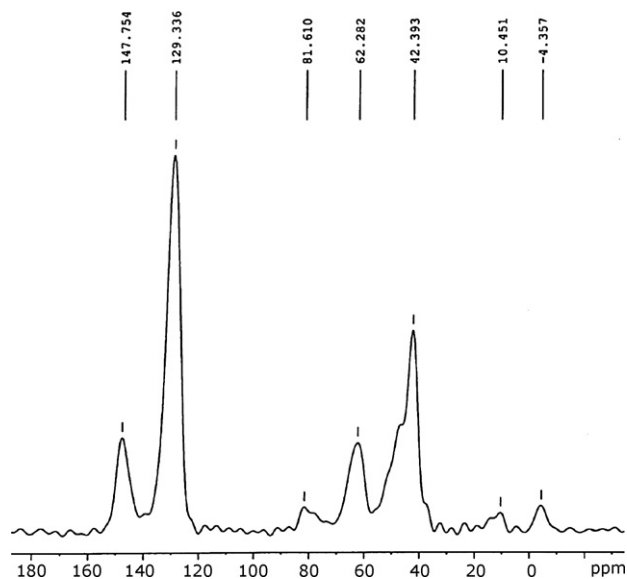


Fig. 2. ^{13}C NMR spectrum of PSTTACMB.

PSTTACMB catalyst. Chou and Weng [39] reported similar type of surface-morphology studies for the polymer-supported catalysts. Balakrishnan and Murugan [37] observed similar analogy results in surface-enriched polymer-supported PTCs. Similarly, the presence

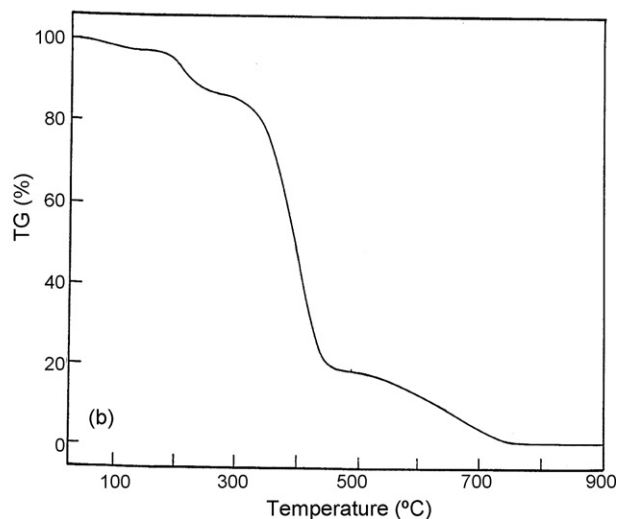
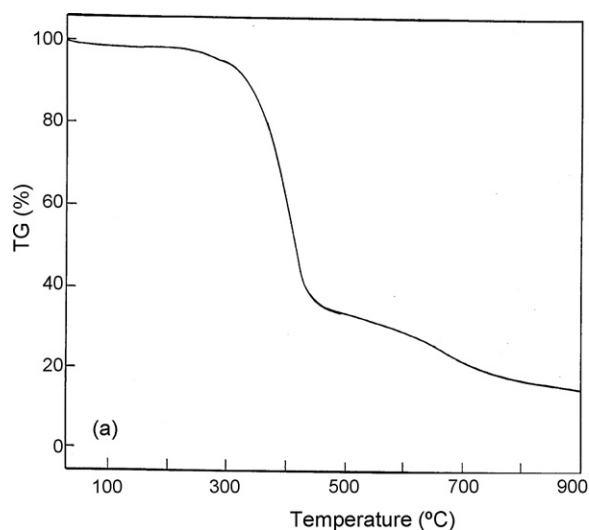


Fig. 3. TGA of (a) single-site PSBTEAC and (b) tri-site PSTTACMB.

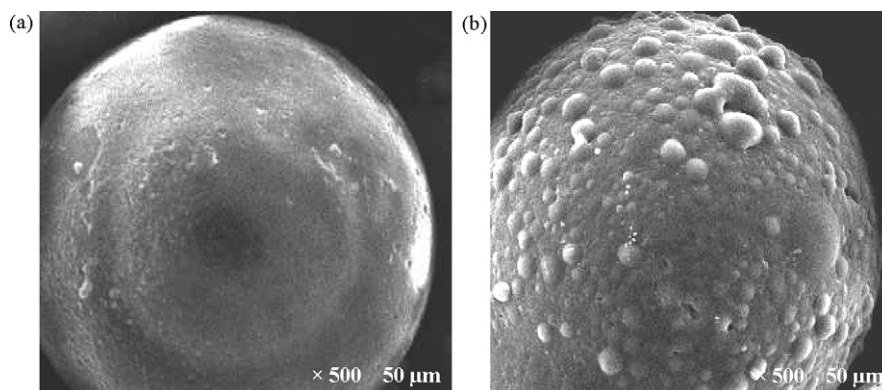


Fig. 4. SEM images of single-bead view (magnified) of (a) single-site PSBTEAC and (b) tri-site PSTTACMB.

Table 1
[Cl⁻] and k_{obs} for PSBTEAC and PSTTACMB.

S. no.	Name of PTCs	[Cl ⁻] mequiv.g ⁻¹			$k_{\text{obs}} \times 10^{-3} \text{ min}^{-1}$
		Theoretical	Volhard	TGA	
1.	Control	–	–	–	No reaction
2.	PSBTEAC	1.35	1.12	1.24	3.59
3.	PSTTACMB	3.05	2.79	2.88	9.38

of number of active sites was also determined from the appearance of tiny nodules on the surface of insoluble six-site PS-MPTC [30].

3.2. Kinetic study

3.2.1. Effect of stirring speed

The effect of stirring speed on the rate of C-alkylation of dihydrocarvone using 1-bromobutane was studied in the range of 100–800 rpm. The pseudo order rate constants were evaluated from the plots of $\log(a-x)$ versus time. The observed reaction rate increases with increase in the stirring speed (Fig. 5) i.e. to start with, the observed rate constant gradually increased from 100 to 500 rpm and then there is a sharp increase at 600 and reaches a maximum at 700 rpm. Further increase of stirring speed (above 700 rpm) does not increase the rate constant and remains constant. The reason for observation of this kind of trend must attributed to the following facts.

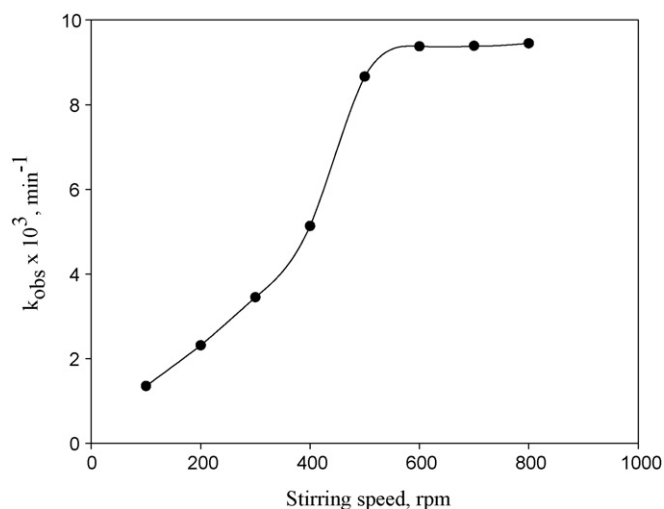


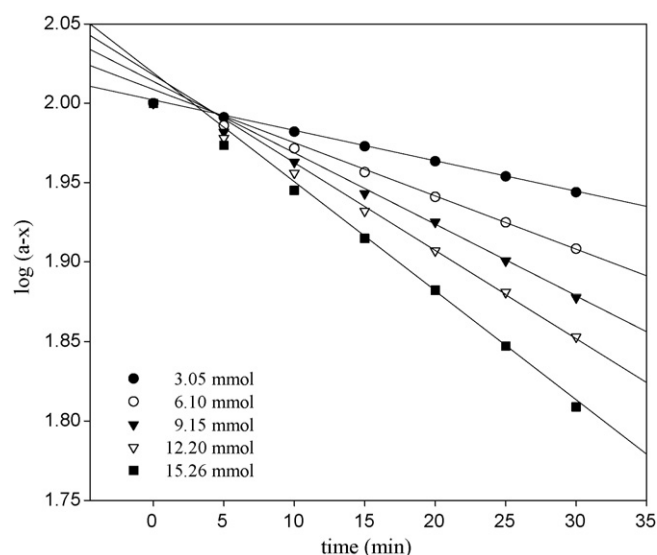
Fig. 5. Effect of stirring speed.

- (i) Increase of perfect collisions between the substrate and catalyst from 100 to 500 rpm and then reaches the maximum collision at 600 rpm.
- (ii) Increase in the interfacial mass transfer area per unit volume of dispersion.
- (iii) Effective mass transformation of Q^+OH^- ion-pair from 500 to 600 rpm.
- (iv) No higher effective mass transfer of Q^+OH^- occurs after 600 rpm.

The rate constant is dependent on the stirring speed up to 600 rpm and then maintains constancy beyond this limit. At stirring speed of 600 rpm, the exchange equilibrium between the anions in the aqueous phase and those associated with quaternary salt in the organic phase must be very fast on compared with the displacement reaction and thus the substrate consumption rate becomes independent of stirring rate. Similar observation was reported by Landini et al. [40] in the study of *n*-octylmethane sulfonate catalyzed by quaternary salts Q^+X^- under PTC conditions in a chlorobenzene–water two-phase system. In our case, at below 600 rpm, there is no effective mass transfer of the reacting anion and hence the reaction must proceed via diffusion controlled kinetics. This behavior is in sharp contrast to reactions operative through extraction mechanism, where the reaction rate is directly proportional to the stirring speed. Similar trend was observed by Balakrishnan et al. [41] in the kinetic study for C-alkylation of phenylacetone using *n*-butylbromide catalyzed by aqueous NaOH and BTEAC. When the mass transfer is rate limiting, the reaction rates are directly proportional to the catalytic surface area of the polymeric catalyst and inversely proportional to the radius of spherical catalysts particle [42]. Wang et al. [20] reported the similar trend of observation in the etherification reaction in which the rate of the reaction enhanced up to 600 rpm and at above 600 rpm the rate constants reach constant values. Hence, the independence of the reaction rate constants on the stirring speed above 600 rpm observed in the present study is indicative evidence that the reaction has proceeded via interfacial mechanism. Therefore, 600 rpm is fixed as an optimum stirring speed for further kinetic variations.

3.2.2. Effect of [substrate]

The concentration of substrate was varied in the range of 3.05–15.26 mmol, and keeping the other reagents such as 1-bromobutane and NaOH as constant. The observed rate constants were found to increase on increasing the concentration of dihydrocarvone (Fig. 6). This is because, the presence of more number

Fig. 6. Effect of substrate on k_{obs} .

of active sites in PSTTACMB as well as high concentration of substrate had co-operatively accelerate the reaction and thus increases the probability of meeting the substrate with active sites of catalyst which in turn reflected the observations of increased rate constant. In other words, though the molar ratio of substrate with respect to catalyst increases, at the same time, due to free availability of multi-catalytic active sites at the interface, the rate constant is found to increase as the substrate concentration increases. Balakrishnan et al. [41] observed a similar dependency of rate constant on the substrate concentration in C-alkylation of phenylacetone with *n*-bromobutane. Jayachandran et al. [43] studied the kinetics of Darzen's condensation of chloroacetonitrile with cyclohexanone using aqueous NaOH in the presence of MPTC and suggested that the observed rate constants increase as the amount of substrate increases.

3.2.3. Effect of [catalyst]

The effect of catalyst concentration on the overall reactivity was studied by varying the catalyst amount ranging from 0.56 to 1.30 mequiv. of $[\text{Cl}^-]$ maintaining the other parameters as constant. The rate constants were calculated from the plots of $\log(a-x)$ versus time (Table 2). The observed rate constants of the reaction are found to be proportional to the concentration of catalyst. These data show that there is a linear relationship between the rate of C-alkylation of dihydrocarvone and catalyst concentration. This is quite obvious, because more amount of multi-active site catalyst has increased the number of active sites linearly in the reaction system and thus it maximizes the amount of aqueous phase anions bound to the catalyst cations. A bi-logarithmic plot of the reaction rate constant versus the concentrations of catalyst gave a straight line having a slope of 0.9. Control experiments in the absence of catalyst were also carried out and no product was detected even after 3 h of the reaction.

Table 2
Effect of variation of [catalyst].

$[\text{Cl}^-]$ mequiv.	$k_{\text{obs}} \times 10^{-3}, \text{min}^{-1}$	$4 + \log[\text{Cl}^-]$	$3 + \log k_{\text{obs}}$
0.56	7.24	0.7455	0.8597
0.74	9.35	0.8104	0.9722
0.93	11.61	0.9673	1.0648
1.11	13.56	1.0531	1.1323
1.30	15.50	1.1134	1.1903

Table 3
Effect of variation of [NaOH].

[NaOH] M	$k_{\text{obs}} \times 10^{-3}, \text{min}^{-1}$	$\log[\text{NaOH}]$	$3 + \log k_{\text{obs}}$
2.77	2.19	0.4425	0.3404
4.41	3.27	0.6444	0.5146
6.25	6.66	0.7959	0.8235
8.33	9.36	0.9206	0.9722
10.71	12.79	1.0298	1.1069

Normally, the rate of the reaction catalyzed by insoluble polymer-supported catalysts is limited by the following factors. (i) Mass transfer of the reactants from bulk organic phase to the exterior surface of catalyst particles. (ii) Diffusion of the reactants from the surface of the active catalytic site. (iii) The chemical reaction by intrinsic reactivity at the active site. (iv) Diffusion of products away from the active site to the catalyst particle surface. (v) Mass transfer of products from the catalyst surface into the bulk solution. In the present study, since the rate constants are proportional to the weight (moles) of the added catalyst, the rate-limiting step must have taken place at active sites of the catalyst. Molinari et al. [44] observed a similar dependence of the pseudo-first order rate constants on the amount of heterogenized phosphonium groups in the Br–I exchange reaction of 1-bromooctane. Regen [45] investigated the kinetics of cyanide displacement reaction under triphase conditions and demonstrated that the rate of the reaction was linearly dependent on the amount of catalyst added. A linear dependence of rate constants on the catalyst amount was observed by Yang et al. [46] in the alkylation of ethyl 2-bromoisobutyrate with potassium 4-benzyloxyphenoxide under solid–liquid PTC conditions.

3.2.4. Effect of [NaOH]

In a phase-transfer catalytic reaction by quaternary ammonium salt, the reaction rate is highly affected by the alkaline concentration. The dependence of the reaction rate on the concentration of NaOH in aqueous phase was studied over the range of 2.77–10.71 M. It can be seen that the rate constants increased tremendously with the rise of concentration of NaOH (Table 3). This observation shows that the C-alkylation is highly dependent on the amount of NaOH, and the reaction also follows a pseudo-first-order rate law. The amount of alkoxides, the distribution of the active catalysts and the hydration number of the active catalysts are all affected by the addition of NaOH. These three factors in turn contributed for the enhancement of the C-alkylation reaction rate. The main reason is that on increasing the concentration of alkaline, the hydroxide ion is less solvated by water molecules i.e. the hydration of OH^- is minimized and as a result the activity of OH^- is increased. Therefore, at higher alkaline concentration the rate of C-alkylation is much higher than that of low concentration of NaOH. Chiellini and co-workers [47] reported that the rate of ethylation of PAN with TBAB increased at high concentration of hydroxide ion and have proposed an interfacial mechanism. In the study of phenoxide allylation in a phase-transfer catalytic system, Wu and Lai [48] observed that the extraction of phenol (using PTC) is more effective if the base concentration is higher. A bi-logarithmic plot of the reaction rate against sodium hydroxide concentrations gives a straight line having a slope of 1.4. In the study of C-alkylation of phenylacetone with n-butylbromide using MPTC [49], the kinetic order with respect to aqueous NaOH concentration was found to be 2.0.

3.2.5. Effect of temperature

The effect of varying the temperature on the rate of C-alkylation of dihydrocarvone was studied in the temperature range 313–353 K. The kinetic profile of the reaction is obtained by plotting $\log(a-x)$ versus time. From the plot, it is clear that the rate constants increase with increase in the temperature (Fig. 7). Molinari et al. [50], Tomoi

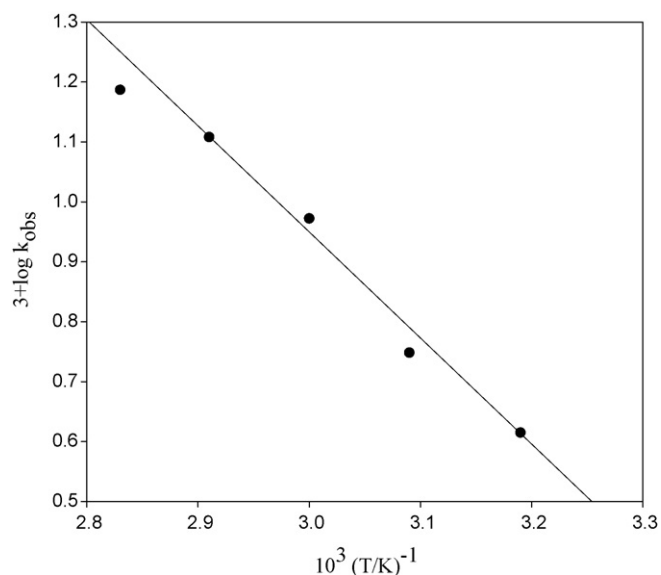


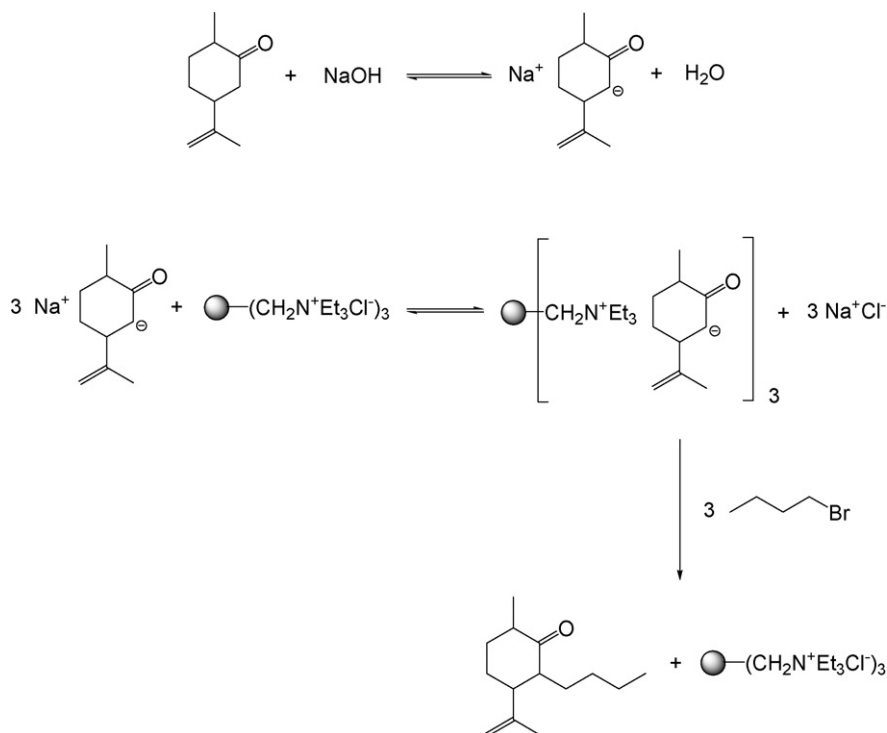
Fig. 7. Arrhenius plot: effect of temperature on the rate of reaction.

and Ford [51] and Lin and Yang [52] also observed analogous temperature dependence in different alkylation reactions. The energy of activation is calculated from the Arrhenius plot, $E_a = 14.2 \text{ kcal mol}^{-1}$. The other thermodynamic parameters, entropy of activation (ΔS^\ddagger), enthalpy of activation (ΔH^\ddagger) and free energy of activation (ΔG^\ddagger) were calculated from Eyring's equation and the obtained values are $13.5 \text{ kcal mol}^{-1}$, $-9.3 \text{ cal K}^{-1} \text{ mol}^{-1}$ and $17.3 \text{ kcal mol}^{-1}$ respectively.

A higher E_a value of $21.5 \text{ kcal mol}^{-1}$ has been reported for the polystyrene bound trimethylammonium ion catalyzed reaction, which was controlled by strict intrinsic reactivity under triphase conditions [33]. Tomoi and Ford [51] also reported the activation energy for the heterogeneous ethylation of phenylacetone nitrile as $20.0 \text{ kcal mol}^{-1}$ and proposed an interfacial mechanism. The E_a value for the alkylation of pyrrolidine-2-one under solid/liquid PTC in presence of potassium carbonate was reported to be $12.4 \text{ kcal mol}^{-1}$ and an interfacial mechanism was proposed [53]. In a comprehensive study of the synthesis of 4-bromophenyl allyl ether [48], it has been observed that the conversion of allyl bromide increases with increase of temperature and the E_a value was found to be $12.5 \text{ kcal mol}^{-1}$. Yadav and Bisht [54] reported an E_a value of $14.0 \text{ kcal mol}^{-1}$ for the etherification reaction between β -naphthol and benzyl chloride in the presence of NaOH and tetrabutylammonium bromide (TBAB). In the present investigation, the continuous increase in the rate constant values on stirring speed from 100 to 600 rpm and the higher activation energy value were indicative of the interfacial mechanism operative under the specified experimental conditions.

3.2.6. Mechanism (Scheme 3)

In the present investigation, the dependency of rate of C-alkylation of dihydrocarvone on stirring speed, [catalyst], [NaOH], temperature and the higher activation energy (E_a) has suggested that the reaction proceeds through interfacial mechanism. The interfacial mechanism for the reactions of carbanions with a variety of electrophiles was proposed by Makosza [55]. A crucial point is the formation of the carbanion by proton abstraction from the CH acid dissolved in a nonpolar solvent by the concentrate aqueous NaOH at the phase boundary. The generated carbanions, as sodium derivatives, remain adsorbed at the surface of the aqueous phase. They cannot migrate into the organic phase because of their low solubility or into the aqueous phase due to the strong



Scheme 3. Mechanism of C-alkylation of dihydrocarvone.

salting-out effect. The catalyst, a lipophilic cation, exchanges anions at the interface, and the new “fully lipophilic” ion-pair migrates into the organic phase where the reaction occurs. The free catalyst can, again, undergo the ion exchange at the interface. Rabinovitz et al. [56] reviewed the interfacial mechanism of hydroxide ion initiated alkylation in presence of PTC. In view of the early results and observation, the mechanism for C-alkylation of dihydrocarvone with 1-bromobutane under triphase conditions involves the following steps:

- (i) The organic phase substrate dihydrocarvone is deprotonated at the interface by the aqueous phase NaOH and forming an ion-pair $[\text{Na}^+\text{R}^-]$.
- (ii) This ion-pair $[\text{Na}^+\text{R}^-]$ at the interface reacts with the catalyst PSTTACMB (Q^+Cl^-) to form $[\text{Q}^+\text{R}^-]$ catalyst-anion pair.
- (iii) The paired anion $[\text{Q}^+\text{R}^-]$ moved into the organic phase and then reacts with the alkylating agent 1-bromobutane to form the alkylated product methyl 2-((oxiran-2-yl)methoxy)benzoate and the catalyst return to its original form of Q^+Cl^- (org).

3.2.7. Reusability of the PSBTTEACHPE catalyst

The reusability of the insoluble tri-site PSTTACMB catalyst was studied by conducting the same C-alkylation of dihydrocarvone reaction. The observed rate constant shows that there is no loss in activity even after recycling the catalyst for 5 times. The quaternary ammonium salts are normally got decomposed and side reactions may occur particularly at high concentration of NaOH. In the present study, the alkylation reaction was conducted using low concentration of NaOH (25%, w/w) and the catalytic activity remains unchanged even after five cycles.

4. Conclusion

A new efficient insoluble polymer-supported tri-site phase transfer catalyst has been successfully synthesized through simplified procedure. The appearance of C–N stretching with high

intensity in FT-IR, the peaks corresponding to methyl and methylene carbons of triethylamine groups observed in ^{13}C NMR, increase in chloride ion concentration determined through Volhard method, increase in the weight loss value of triethylamine group noticed in TGA, availability of heterogeneous tiny nodules observed in SEM images and the enhanced rate constant in the C-alkylation of dihydrocarvone have all proved that the new insoluble MPTC viz., PSTTACMB should contain approximately three active sites as compared with the single-site PSBTEAC. The rate constants observed from the kinetic study of C-alkylation of dihydrocarvone using the superior PSTTACMB are dependent on each variable such as stirring speed, [substrate], [catalyst], [NaOH] and temperature. The activation energy E_a and thermodynamic parameters viz., ΔS^\ddagger , ΔH^\ddagger and ΔG^\ddagger values were calculated and reported as $14.2 \text{ kcal mol}^{-1}$, $13.5 \text{ kcal mol}^{-1}$, $-9.3 \text{ cal K}^{-1} \text{ mol}^{-1}$ and $17.3 \text{ kcal mol}^{-1}$ respectively. An interfacial mechanism was suggested for the C-alkylation of dihydrocarvone. The insoluble PSTTACMB catalyst can be reused and there is no loss in activity was observed upto five cycles.

Acknowledgements

The financial assistance provided by UGC, New Delhi, Government of India is gratefully acknowledged. One of the authors P.G is thankful to CSIR, New Delhi for providing SRF.

References

- [1] C.M. Starks, C.L. Liotta, M. Halpern, Phase-Transfer Catalysis: Fundamentals, Applications and Industrial Perspectives, Chapman and Hall Publications, New York, USA, 1994.
- [2] E.V. Dehmlow, S.S. Dehmlow, Phase Transfer Catalysis, 3rd ed., VCH, New York, USA, 1993.
- [3] Y. Sasson, R. Neumann (Eds.), Handbook of Phase Transfer Catalysis, Blackie Academic and Professional, London, UK, 1997.
- [4] A.W. Herriott, D. Picker, J. Am. Chem. Soc. 97 (1975) 2345–2349.
- [5] A. Brandstrom, Adv. Phys. Org. Chem. 15 (1977) 267–330.
- [6] S.L. Regen, J. Am. Chem. Soc. 97 (1975) 5956–5957.
- [7] V. Ragaini, G. Colombo, P. Barzhagi, E. Chiellini, S. D'Antone, Ind. Eng. Chem. Res. 29 (1990) 920–924.

- [8] V. Ragaini, G. Colombo, P. Barzhagi, *Ind. Eng. Chem. Res.* 27 (1988) 1382–1387.
- [9] P. Schlunt, P.C. Chau, *J. Catal.* 102 (1986) 348–356.
- [10] W.M. MacKenzie, D.C. Sherrington, *Polymer* 22 (1981) 431–433.
- [11] M. Tomoi, M. Ikeda, H. Kakiuchi, *Tetrahedron Lett.* 39 (1978) 3757–3760.
- [12] S. Desikan, L.K. Doraiswamy, *Chem. Eng. Sci.* 55 (2000) 6119–6127.
- [13] S. Baj, A. Siewniak, B. Socha, *Appl. Catal. A: Gen.* 309 (2006) 85–90.
- [14] J.P. Idoux, R. Wysocki, S. Young, J. Turcot, C. Ohlman, R. Leonard, *Synth. Commun.* 13 (1983) 139–144.
- [15] T. Balakrishnan, J.P. Jayachandran, *J. Chem. Soc., Perkin Trans. 2* (1995) 2081–2085.
- [16] M. Benaglia, M. Cinquini, F. Cocci, G. Tocco, *Tetrahedron Lett.* 43 (2002) 3391–3393.
- [17] M.L. Wang, Y.M. Hsieh, *J. Mol. Catal. A: Chem.* 210 (2004) 59–68.
- [18] M.L. Wang, Z.F. Lee, *Ind. Eng. Chem. Res.* 45 (2006) 4918–4926.
- [19] M.L. Wang, Y.H. Tseng, *React. Kinet. Catal. Lett.* 82 (2004) 81–87.
- [20] M.L. Wang, Z.F. Lee, F.S. Wang, *J. Mol. Catal. A: Chem.* 229 (2005) 259–269.
- [21] T. Balakrishnan, E. Murugan, A. Siva, *Appl. Catal. A: Gen.* 273 (2004) 89–97.
- [22] E. Murugan, A. Siva, *J. Mol. Catal. A: Chem.* 235 (2005) 220–229.
- [23] A. Siva, E. Murugan, *J. Mol. Catal. A: Chem.* 241 (2005) 101–110.
- [24] E. Murugan, P. Gopinath, *J. Mol. Catal. A: Chem.* 294 (2008) 68–73.
- [25] E. Murugan, A. Siva, *Synthesis* (2005) 2022–2028.
- [26] A. Siva, E. Murugan, *J. Mol. Catal. A: Chem.* 241 (2005) 111–117.
- [27] A. Siva, E. Murugan, *Synthesis* (2005) 2927–2933.
- [28] A. Siva, E. Murugan, *J. Mol. Catal. A: Chem.* 248 (2006) 1–9.
- [29] E. Murugan, P. Gopinath, *Appl. Catal. A: Gen.* 319 (2007) 72–80.
- [30] E. Murugan, A. Siva, *J. Mol. Catal. A: Chem.* 277 (2007) 81–92.
- [31] P. Srivastava, R. Srivastava, *Tetrahedron Lett.* 48 (2007) 4489–4493.
- [32] M.A. Sprecker, M.R. Harma, International Flavors and Fragrances Inc., Brit. U.K. Pat. Appl. GBB2139222, U.S. Appl. 487045, *Chem. Abstr.* 102, P220567e (1982).
- [33] R.D. Acker, *Tetrahedron Lett.* 19 (1978) 2399–2402.
- [34] P.A. Wender, M.A. Eissenstat, *J. Am. Chem. Soc.* 100 (1978) 292–294.
- [35] Y. Tanigawa, H. Ohta, A. Sonoda, S.I. Murahashi, *J. Am. Chem. Soc.* 100 (1978) 4610–4612.
- [36] H.O. House, M.J. Umen, *J. Org. Chem.* 38 (1973) 1000–1003.
- [37] T. Balakrishnan, E. Murugan, *J. Polym. Sci. Part A: Polym. Chem.* 42 (2003) 347–364.
- [38] H.S. Wu, C.S. Lee, *J. Catal.* 199 (2001) 217–223.
- [39] S.C. Chou, H.S. Weng, *J. Appl. Polym. Sci.* 39 (1990) 1665–1679.
- [40] D. Landini, A. Maia, F. Montanari, *J. Am. Chem. Soc.* 100 (1978) 2796–2801.
- [41] T. Balakrishnan, K. Arivalagan, R. Vadukut, *Ind. J. Chem.* 31B (1992) 338.
- [42] C.M. Starks, C.L. Liotta, *Phase Transfer Catalysis*, Academic Press, New York, 1978 (chapter 2).
- [43] J.P. Jayachandran, T. Balakrishnan, M.L. Wang, *J. Mol. Catal. A: Chem.* 152 (2000) 91–98.
- [44] H. Molinari, F. Montanari, S. Quici, P. Tundo, *J. Am. Chem. Soc.* 101 (1979) 3920–3927.
- [45] S.L. Regen, *J. Am. Chem. Soc.* 98 (1976) 6270–6274.
- [46] H.M. Yang, P.I. Wu, C.M. Li, *Appl. Catal. A: Gen.* 193 (2000) 129–137.
- [47] R. Solaro, S.D. Antone, E.J. Chiellini, *J. Org. Chem.* 45 (1980) 4179–4183.
- [48] H.S. Wu, J.J. Lai, *Ind. Eng. Chem. Res.* 34 (1995) 1536–1538.
- [49] T. Balakrishnan, J.P. Jayachandran, in: M.E. Halpern (Ed.), *ACS Symposium Series*, vol. 659, ACS, Washington, DC, 1997, 277 pp. (chapter 21).
- [50] H. Molinari, F. Montanari, P. Tundo, *J. Chem. Soc. Chem. Commun.* (1977) 639–641.
- [51] M. Tomoi, W.T. Ford, *J. Am. Chem. Soc.* 103 (1981) 3821–3828.
- [52] P.J. Lin, H.M. Yang, *J. Mol. Catal. A: Chem.* 235 (2005) 293–301.
- [53] Y. Sasson, N. Bilman, *J. Chem. Soc., Perkin Trans. 2* (1989) 2029–2033.
- [54] G.D. Yadav, P.M. Bisht, *J. Mol. Catal. A: Chem.* 223 (2004) 93–100.
- [55] M. Makosza, *Pure Appl. Chem.* 43 (1975) 439–462.
- [56] M. Rabinovitz, Y. Cohen, M. Halpern, *Angew. Chem. Int. Ed. Engl.* 25 (1986) 960–970.