



NEW POLYMER-SUPPORTED MULTI-SITE PHASE TRANSFER CATALYST IN DICHLOROCARBENE ADDITION TO STYRENE

P. Gopinath* & E. Murugan**

* Department of Chemistry, Alpha College of Engineering, Udayavar Koil Street, Thirumazhisai, Poonamalle, Chennai, Tamilnadu

** Department of Physical Chemistry, School of Chemical Sciences University of Madras, Guindy Campus, Chennai, Tamilnadu

Abstract:

A new insoluble polymer-supported multi-site phase transfer catalyst containing two active sites was synthesized by simplified procedure. This di-site polymer-supported PTC was characterized by FT-IR, ¹³C NMR, TGA, chloride ion & SEM analyses. Similarly, polymer-supported single-site catalyst was also prepared with the same catalytic moiety. The catalytic efficiency was ascertained through dichlorocarbene addition to styrene under pseudo-first order reaction conditions. The rate constants were calculated by following the disappearance of styrene through Gas Chromatography. It was found that the di-site PS-PTC was more effective than single-site PS-PTC in terms of rate constant. The kinetic variables such as stirring speed, [substrate], [NaOH], [catalyst], and temperature were thoroughly studied. The thermodynamic parameters viz., activation energy, enthalpy, entropy and free energy change were also calculated. Based on the observed kinetic and thermodynamic results, an interfacial mechanism was proposed.

Key Words: Multisite, Dichlorocarbene, Styrene & Interfacial Mechanism

1. Introduction:

Generally the reactions between two immiscible substrates are difficult to carry out because they do not contact each other. Phase transfer catalysis (PTC) is a well-known technique to carry out these types of reactions at high rate. PTCs available in soluble form are immensely popular due to their commercial availability and easy reaction work-up. But the main drawback of soluble PTC is the recovery of catalyst from product is very difficult. This problem can be overcome by attaching the catalyst to an insoluble polymer and it is known as polymer-supported PTC reported by Regen. These catalysts can be easily recovered by simple filtration and reused again which makes them useful for continuous reactors like packed bed reactors. Though, there were numerous soluble and insoluble single-site PTC's reported in literature, they were not catalyzed the reaction efficiently because they contain only one active site. Also, large quantity of these single-site catalysts required to carry out the reactions efficiently in short period of time. The important considerations in the selection of the catalyst are economy of scale and efficiency, specifically on the industrial scale. In order to satisfy these needs effectively, polymer-supported multi-site PTCs containing more than one active site have been developed.

Idoux et al. was the first who synthesized high-activity multi-site phosphonium PTC containing three active sites as soluble and insoluble polymer-supported catalysts and reported their catalytic activity using simple S_N2 reaction and some weak nucleophile-electrophile S_NAr reactions. Balakrishnan et al. reported the synthesis of soluble ammonium PTC containing two and three active sites which are used for various alkylations and carbene additions. Benaglia et al. reported the synthesis of a poly (ethylene glycol)-supported tetra-kis ammonium salt as a recyclable PTC and found that an increase in the number and a proper spatial arrangement of the catalytic sites thus

providing more efficient catalyst. The total weight of MPTC required in these reactions is less compared to related single-site PTCs and also no doubt that the number of catalytic site can decide the efficiency of reaction which in turn controls the economy of the reaction process. In our laboratory, we also reported many insoluble polymer-supported PTCs and their efficiency in alkylation, condensation and addition reactions. Dichlorocarbene addition to any olefins produced dihalocycloderivatives, which on further treatment with magnesium or sodium and converted to a number of other valuable products. Literature reports on the generation and reaction of dichlorocarbene stress the necessity of operating under strictly anhydrous conditions, because of the ready and rapid hydrolysis of dichlorocarbene. Many of these difficulties are eliminated when the reactions are carried out in biphasic systems in the presence of PTC and concentrated NaOH. Makosza et al. were the first to prepare dichlorocyclopropane under phase transfer condition successfully. Several reports are available for generation of dichlorocarbene to various olefins using PTC.

2. Experimental:

i) Chemicals:

Gelatin (Lancaster), boric acid (SRL), polyvinyl alcohol (Lancaster), styrene (Lancaster), vinylbenzylchloride (Lancaster), divinylbenzene (Lancaster), AIBN (Lancaster), 3,5-dimethyl phenol (Lancaster), sulfuryl chloride (SRL), potassium carbonate (Merck), tetrahydrofuran (SRL), triethylamine (SRL), acetonitrile (SRL), methanol (SRL) and acetone (SRL) were used as provided.

ii) Instrumentation:

The FT-IR spectra were recorded on a Bruker-Tensor 27 FT-IR spectrophotometer. The solid ^{13}C NMR spectrum was recorded using AMX-400 MHz spectrometer. Thermogravimetric analysis (TGA) was carried out in a ZETZSCH-STA 409C thermal analyzer. Surface morphology study was performed using JEOL JSM-6360 scanning electron microscope (SEM). Kinetics of dichlorocarbene addition to styrene 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, 3m \times 1/8 in. stainless steel tube.

iii) Preparation of insoluble di-site PC viz., polymer supported 3,5-bis(triethyl ammonium methylene chloride) benzene (PSBBTEACB)

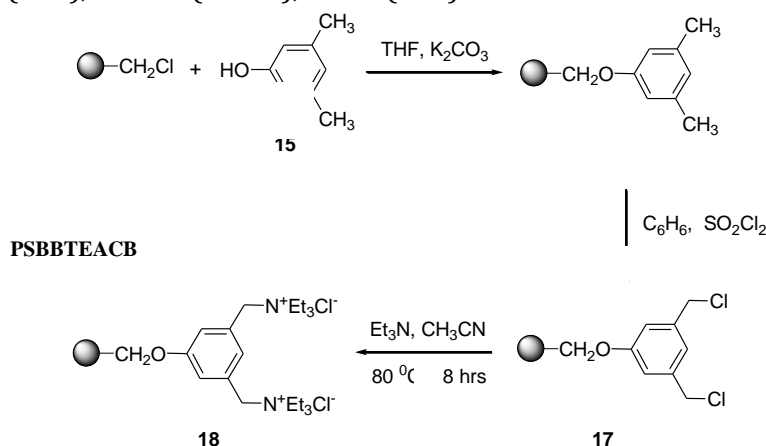
The procedure for the preparation of di-site PTC (PSBBTEACB) was already reported in the literature. Initially, the cross-linked copolymer beads were prepared by conducting the polymerization reaction using vinylbenzylchloride (25%, 0.27 mol) as a functional monomer, divinylbenzene (2%, 0.04 mol) as a cross-linking monomer and styrene (73%, 1.13 mol) as a supporting monomer via suspension polymerization technique. From the obtained cross-linked copolymer beads, 2 g (+120 –140 mesh size) were swelled in THF (20 ml) for about 24 hrs. Then 3,5-dimethyl phenol (4 g) 15 and K_2CO_3 (1 g) were added and the mixture was refluxed at 70 °C using oil bath for 36 hrs in an inert atmosphere. The resulting condensed polymer beads were filtered and then washed with THF, methanol and acetone and dried in oven at 60 °C for about 24 hrs. The dried beads were chlorinated by stirring with sulfuryl chloride (25 ml) in benzene for 48 hrs at 70 °C.

The resulting beads were collected, washed with benzene, acetone and dried. Finally, the chlorinated beads were quaternized with excess of triethylamine (20 ml) and acetonitrile in an inert atmosphere at 80 °C for 72 hrs. The quaternized di-site PTC

viz., PSBBTEACB was filtered and washed with methanol, acetone and dried at 60 °C for about 18 hrs.

[Cl⁻] : 2.4 mequiv. g⁻¹ (Volhard's method)

FT-IR : 2922 (C-H), 10674 (C-O-C), 1154 (C-N).



iv) 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 experiments for dichlorocarbene addition to styrene (Scheme 2) catalyzed by PSBBTEACB and single-site PSBTEAC in the presence of aqueous sodium hydroxide were carried out by the reverse addition method i.e. delayed addition of chloroform. The substrate styrene (6.1 mmol), aqueous NaOH 10% (w/w) (25 ml), hexadecane (1 ml) and the respective catalysts single/tri-site containing 0.74 mequiv. of [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 chloroform 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 5min). The kinetics of the reaction was followed by estimating the disappearance of styrene using gas chromatograph. The column (5% SE-30 chrom WIHP 80/100, 3m×1/8 in. stainless steel packed column) was maintained at 200 °C. For every sample, 0.5µl 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: styrene (1.17min), chloroform (0.70 min) and dichlorocyclopropane product (2.79 min). The pseudo-first order rate constants were calculated from the plots of log (a-x) versus time.

3. Results and Discussion:

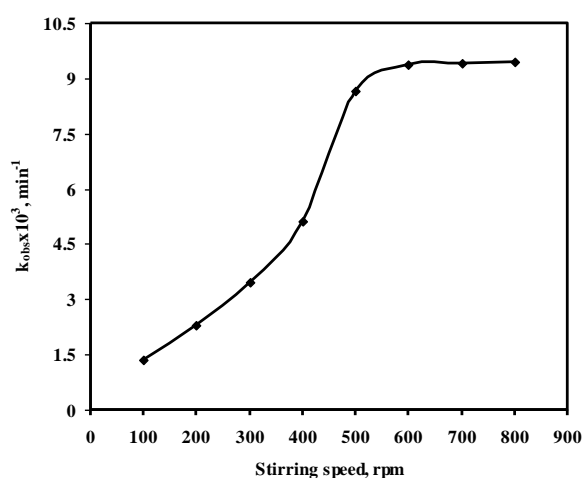
i) Characterization of PSBBTEACB:

The availability of two active-sites in the new di-site PSBBTEACB was established from the appearance of sharp peak at 1171 cm⁻¹ for C-N stretching in FT-IR spectrum. In ¹³C NMR spectrum, the peaks found at 10.4 and 42.3 ppm corresponds to quaternized methyl and methylene carbons of PSBBTEACB proved the presence of active sites. The amount of functional groups (triethylamine) present in the catalyst quantitatively proved by measuring its weight loss at 160 – 200 °C. Similarly, the presence of tiny nodules on the surface of PSBBTEACB by SEM analysis also proved the more number of active sites in the catalyst.

ii) Kinetic Study:

a) Effect of Stirring Speed:

In order to ascertain the influence of stirring speed to mass transfer of reactants to the catalyst surface, the speed of agitation was varied from 100 to 800 rpm for the dichlorocarbene addition to styrene. The experimental results show that the observed reaction rate increases with increase in the stirring speed i.e. to start with, the observed rate constant gradually increased from 100 to 400 rpm and then there is a sharp increase at 500 and reaches a maximum at 600 rpm. Further increase of stirring speed at above 600 rpm does not increase the rate constant and remains constant. Balakrishnan et al. observed a similar trend of results in dichlorocarbene addition to styrene. Similar observation was reported by Wang et al. who studied the kinetics of dichlorocyclopropanation of 4-vinyl-1-cyclohexene using a soluble two-site PTC in which the rate constants depend on stirring speed even when it is greater than 1000 rpm. Rajendran et al. also reported the dependence of stirring speed on the rate of reaction upto 700 rpm for dichlorocarbene addition to allyl phenyl ether.



b) Effect of [Substrate]:

Kinetic experiments were performed by varying the concentration of styrene ranging from 5 - 25 mmol, maintaining the other parameters such as chloroform and 10 % w/w NaOH in excess. The rate constants are calculated from the plots of $\log(a-x)$ versus time. A straight line was obtained by plotting the rate constants against the concentration of styrene. The observed rate constants were found to increase when the substrate concentration increases. The increase in rate constants may be attributed to the increase in the ratio of the number of active sites of the catalyst to the corresponding amount of substrate present. Do et al. reported the similar trend of observation in the kinetics of oxidation of benzyl alcohol by hypochlorite ion in the presence of tetrabutylammonium chloride. They found that the reaction rate was increased on increasing the concentration of benzyl alcohol. The same kind of dependency of rate constant on substrate concentration was also observed in the kinetic study of dichlorocarbene addition to citral using a multi-site PTC.

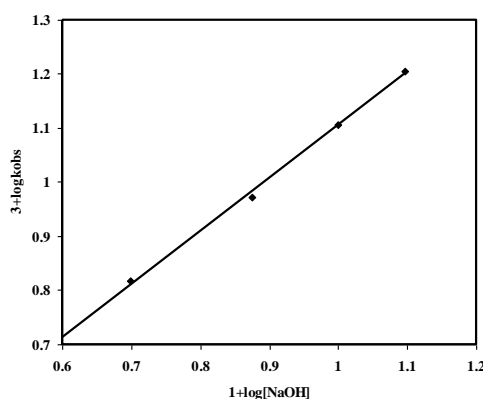
c) Effect of [Catalyst]:

The effect of catalyst concentration was studied in the range of 0.37 to 1.11 m.eq.g⁻¹ of [Cl]. From the plots, it is proved that the rate of reaction is directly proportional to the amount of catalyst. When catalyst concentration increased, the number of active-sites in the reaction also raised due to the presence of two active sites. It provides the effective collision between the substrate and catalyst. As a result, concentration of dichlorocarbene in the organic phase is also raised.

Further, the catalytic efficiency of new catalyst was compared with single-site PS-PTC through dichlorocarbene addition to styrene carried out under identical experimental conditions and the pseudo-first order rate constants were evaluated as 0.45×10^{-3} , min^{-1} . The observed pseudo-first order rate constant indicates that PSBBTEACB has proved to be $\cong 2$ times more active (0.85×10^{-3} , min^{-1}) than single-site PS-PTC. Control experiments was also carried out for dichlorocarbene addition to styrene in the absence of catalyst under specified conditions in which no product was observed even after 3 hrs of reaction. This gives evidence that there is no scope for autocatalysis in the absence of the phase-transfer catalyst. Starks reported similar observation in the study of dichlorocarbene addition to cyclohexene using tridecylmethylammonium chloride as a catalyst. The effect of catalyst structure are very important, especially in dichlorocarbene addition reactions which was explained by Dehmlow's comparative study in the dichlorocarbene addition to cyclohexene using different catalysts with high yields of products. Jayachandran et al. reported the same observation in the dichlorocyclopropanation of dicyclopentadiene by employing aqueous NaOH and chloroform in excess in the presence MPTC. Similar trend in the kinetics of dichlorocarbene addition to styrene under liquid-liquid and solid-liquid PTC conditions and revealed that the reaction follows first order with respect to catalyst concentration.

d) Effect of [NaOH]:

The rate of dichlorocarbene addition is highly influenced by the concentration of alkali in aqueous solution. The reaction rates were measured in the range of 1.31 - 4.41 M NaOH. The observed reaction rate is slow at low concentration, but it becomes very fast at high concentration. This may be due to the increased activity of OH^- ions because they are less solvated by water molecules



In early studies, the systematic kinetic study of dichlorocarbene addition to styrene was performed using benzyltriethylammonium chloride as a catalyst and 50 % NaOH was employed, whereas in the present study, the catalyst was more active even in 10 % NaOH and hence it is the optimum concentration required to get the higher conversions. It is worth to highlight the fact that the lower amount of NaOH is of specific interest in industry as there is a scope of easy reaction work up and durability of the reaction vessels. A similar trend was observed in the kinetic study of dichlorocyclopropanation of styrene in the presence of TEACB as catalyst.

e) Effect of temperature

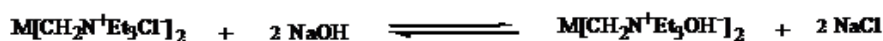
The influence of varying temperature on the rate of reaction of styrene with chloroform was carried out in the temperature range from 303 - 323 K. The reaction rate constants increase with the increase in temperature. From the Arrhenius plot, the

energy of activation is calculated, $E_a = 18.3 \text{ kcal mol}^{-1}$. The other thermodynamic parameters such as ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger were calculated as $17.7 \text{ kcal mol}^{-1}$, $-11.5 \text{ cal K}^{-1} \text{ mol}^{-1}$ and $21.9 \text{ kcal mol}^{-1}$ respectively. Higher activation energy has been reported 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 $13.4 \text{ kcal mol}^{-1}$ and for this an interfacial mechanism has been proposed. In the kinetic study of dichlorocarbene addition to allyl phenyl ether under PTC conditions, the E_a value was reported as $13.99 \text{ kcal mol}^{-1}$ and proposed an interfacial mechanism. Taking into consideration of the earlier studies, the observed energy of activation in the present study for the dichlorocarbene addition to styrene is $18.3 \text{ kcal mol}^{-1}$ and hence the reaction should proceed through an interfacial mechanism.

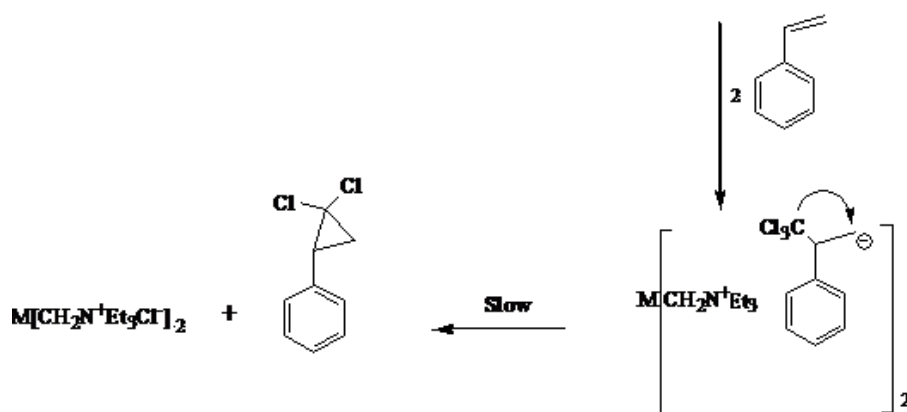
4. Mechanism:

From the observed experimental results, the dependency of kinetic data on the stirring speed up to 800 rpm, concentrations of the catalyst, aqueous hydroxide ions, temperature and higher E_a value strongly proved that dichlorocarbene addition to styrene 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 PTC anion was exchanged by haloderivative to form an active intermediate of PTC/ CCl_3^- which can react with the olefinic group containing styrene to give a dichlorocyclopropanated product. Furthermore, the concentration of catalytic site per molecule is increased from single-site to multi-site (di-site) as a result of that the abstraction of proton from chloroform is more effective than the single-site PTC.

Aqueous Phase



Organic Phase



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