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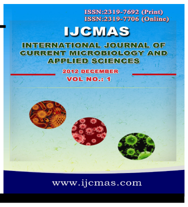

Original Research Article

Dichlorocyclopropanation of α- methyl styrene using phase-transfer Catalyst - A kinetic study

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ABSTRACT

KEYWORDS

Phase transfer catalysis;
Dichlorocyclopropanation;
α- methyl styrene;
Kinetics;
Carbenes;
Interfacial mechanism

In this work, a phase transfer catalyst viz., benzyltriethylammonium chloride (PTC) was assessed by observing the kinetics of dichlorocarbene addition to α- methyl styrene. The formation of the product was monitored by GLC. Dichlorocyclopropanation of α- methyl styrene catalyzed by this carried out in two-phase medium under pseudo-first-order conditions by keeping aqueous sodium hydroxide and chloroform in excess. The effect of various experimental parameters on the rate of the reaction has been studied. From the Arrhenius plot, the activation energy was found to be 16.17 kcal mol^{-1}. Also thermodynamic parameters such as $\Delta S^{\#}$, $\Delta G^{\#}$ and $\Delta H^{\#}$ were evaluated; based on the experimental results, a suitable mechanism is proposed.

Introduction

Conventional techniques (Menger, 1972) for removing the constraints of mutual insolubility of aqueous phase with organic phase are industrially unattractive and polluting. A plausible technique now widely known as ''phase transfer catalysis'' (PTC) has emerged as a broadly useful tool (Starks *et al.*, 1994; Selvaraj and Rajendran, 2011; Li, 1996; Yangand Peng, 2010: Wang and Chen 2010; Omera *et al.*, 2008) in solving the predicament of insolubility of aqueous phase with organic phase. In this methodology, involving a substrate (in the organic layer) and an anionic reagent or a nucleophile (in the aqueous layer), reacting anions are continuously introduced into the organic phase. Currently, PTC is an important choice in organic synthesis and is widely applied in the manufacturing processes of specialty chemicals, such as pharmaceuticals, perfumes, dyes, additives, pesticides, and monomers.

As the use of PTC grew, much effort was placed on the development of phase transfer catalysts with higher catalytic efficiency. In order to cater to these needs, ''multi-site'' phase transfer catalysts (MPTC) have been developed. Salient features of this type of onium salts when compared with single site salts include facile preparation, low energy requirement and high reactivity in a particular synthetic transformation under mild reaction conditions.

Mason (1997) for the first time, synthesized ''multi-site'' phosphonium PTC's as soluble and polymer-supported catalysts. Wang *et al* (2007) and Wang *et al.* (2006) have reported synthesis of multi-site phase transfer catalysts. In recent times, Ali (2007) reported an efficient method for the synthesis of tertiary amines via N-alkylation of amines by a, X-dihaloalkanes using multisite phase-transfer catalysts derived from hydroquinone. Earlier, we reported the synthesis of (Vivekanand and Balakrishnan, 2009.) soluble multi-site onium salts and the efficiency of the same were examined by following the kinetics of C-alkylation. We recently compared (Wang and

Rajendran, 2007) the efficiency of a new MPTC with various single-site phase transfer catalysts in the kinetics of epoxidation addition reactions of olefins. Inspired by the considerable increase in catalytic activity, the MPTC's are becoming more attractive among chemists. We decided to examine its efficiency by studying the kinetics of dichlorocarbene addition of α- methyl styrene under pseudo-first-order reaction conditions (Scheme 1). Thermodynamic parameters of the reaction were also evaluated from the Arrhenius plot and from the experimental results, a plausible mechanism has been proposed. Further, the catalytic efficiency of the PTC is compared with the commercially available single-site PTC's.

Materials and Methods

Materials

α-methylstyrene, Vinylcyclohexane, benzyltriethylammonium chloride (BTEAC), benzyltriethylammonium bromide (BTEAB). tetrabutylammonium chloride (TBAC), tetrabutylammonium bromide (TBAB), sodium hydroxide and chloroform were used as such.

Instrumentation

The IR spectra were recorded on a Bruker-Tensor 27 FT-IR spectrophotometer. The ^{1}H NMR and ^{13}C NMR spectra were recordedon a Bruker 300, JEOL 400 MHz and JEOL 500 MHz spectrometers respectively. The mass spectra were recorded on a Jeol JMS-DX 300 HF mass Spectrometer. Elemental analyses were performed on a Perkin• Elmer 240B elemental analyzer. Gas Chromatographic analyses were performed on aria model 3700, with flame ionization detector and Vista CDS 401 data station. The column used was 5% SE-30 Chrome WHP 80/100, 3 M 1/800 stainless steel tube.

Kinetics of dichlorocarbene addition to α-methyl styrene.

The kinetic measurements were carried out in a smooth-walled 150 mL three-necked flask fitted with flat-bladed stirring paddle and a reflux condenser. All ingredients *viz.*, 20 mL of 30% w/w aqueous NaOH, of the catalyst and 10 mL $CHCl_3$ (Solvent) were added and stirred at 200 rpm for 5 min at 45°C to stabilize the catalyst. α-Methyl styrene (1.0 mL) preheated to 45°C was added to the reaction mixture. The stirring speed was increased to 600 rpm by adjusting the stirring speed with the tachometer. Samples were collected from the organic layer at regular intervals of time. Samples were analyzed using Gas chromatography (Varian 3700 model, Vista CDS 401 data system with flame ionization detector) using the column (5% SE-30 Chrome WHP 80/100, 2 m 1/800 stainless tube length).

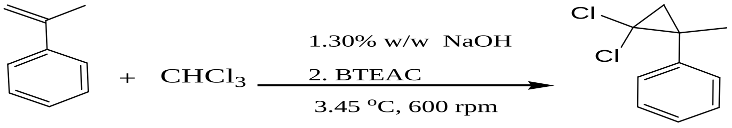
Results and discussion

The kinetic experiments of the dichlorocarbene addition to α-methyl styrene were carried out under pseudo-first order conditions, taking chloroform and aqueous NaOH in excess at 45°C and the pseudo-first order rate constant was calculated by measuring the disappearance of α-methyl styrene through gas chromatography (Scheme 1). The pseudo-first order rate constants were evaluated from the plots of –ln (1-X) versus time.

Influence of varying stirring speed

The effect of varying the stirring speed on the rate of dichlorocarbene addition to α-Methyl styrene reaction using the PTC (BTEAB) was studied in the range of 200–800 rpm. The rate of the reaction increases as the stirring speed increases and levels off to a constant value above the optimum stirring speed, 600 rpm (Fig. 1). Therefore, in order to study the other kinetic variables of the dichlorocarbene addition, we kept the stirring speed at 600 rpm. This type of observation on stirring speed is well documented in early studies (Starks *et al.*, 1994; Wang *et al.*, 2003) and an interfacial mechanism was proposed. Wang *et al* (2006) observed a similar trend in dichlorocarbene addition to styrene and C-alkylation of phenyl acetone using ethyl iodide. A analogous trend was observed by Starks et al. from the kinetic study of cyanide displacement reaction catalyzed by tributylhexadecylphosphonium bromide, wherein the rates were found to be independent of stirring speed>250 rpm.

Scheme 1. Dichlorocyclopropanation of α- methyl styrene catalyzed by BTEAC.



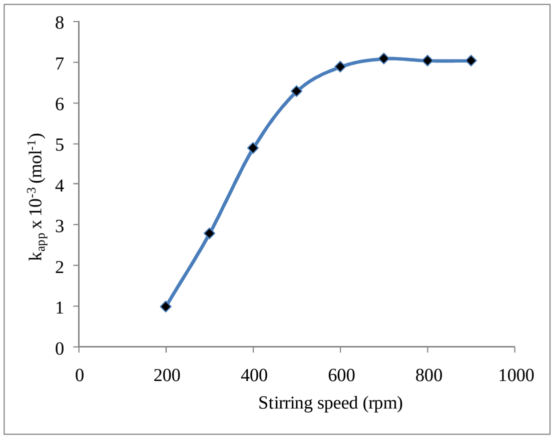
α- methyl styrene

1-(2,2-dichloro-1-methylcyclopropyl)benzene

Influence of catalyst amount

The effect of catalyst amount on the rate of dichlorocarbene addition to α-methyl styrene was studied by varying the catalyst (BTEAC) concentration from 0.08 x10^{-3} to 5.2 x 10^{-3} mmol (based on substrate concentration) and keeping other experimental parameters constant. The rate constants are linearly dependent on the amount of catalyst used in each reaction, which may be attributed to the increase in number of catalytic reactive sites, which in turn would maximize the amount of aqueous phase anions bound to the catalyst cations. It was interesting to observe that only a small catalytic amount (1.6 x 10^{-4} mmol) is required in order to obtain good yields of the dichlorinated product. Starks *et al* (1994) reported an akin observation in the study of dichlorocarbene addition to cyclohexene using tridecylmethylammonium chloride as a PTC. Occurrence of limiting reaction, the linear dependence of the reaction rate constants on the catalyst concentration and active catalyst formation shows that the reaction is believed to proceed through the interfacial mechanism. Wang *et al.* (2007) observed an analogous dependence of pseudo-first-order rate constants on the amount of catalyst for the dichlorocarbene addition to styrene. In the present study, plot of the reaction rate constants versus the concentrations of the catalyst gave a straight line having a slope value of 0.56 (Fig. 2). The significant increase in the yield of dichlorocarbene adducts reflects the ability of the quaternary ammonium salt to affect the **:**CCl_2 to be generated transferred to the organic phase, which was more reactive with the organic substrates than the water molecule.

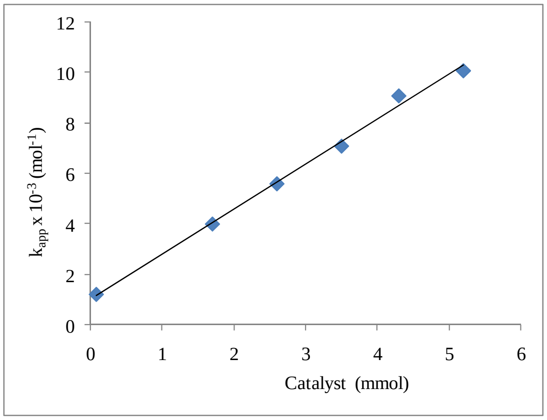
Fig. 1. Dichlorocarbene addition to α- methyl styrene. Dependence of k_{app} on stirring speed.



Comparison of reaction rate constant with various single-site PTC's.

In this work, the phase transfer catalyst and its reactivity was compared with different single-site of the conventional quaternary ammonium salts, such as tetrabutylammonium bromide (TBAB), tetrabutylammonium chloride (TBAC), benzyltriethylammonium bromide (BTEAB) and benzyltriethylammonium chloride (BTEAC) in the dichlorocarbene addition of vinylcyclohexane under identical conditions. A similar trend was observed by Wang *et al* (2003) in the kinetic study of ethoxylation of p-chloronitrobenzene using phase-transfer catalysts. The reaction follows a pseudo-first-order rate law. From the Table1. BTEAB shows greater catalytic activity than TEAB. The following order illustrates the relative catalytic activity of different catalysts in the dichlorocarbene addition reaction of α- methyl styrene: BTEAC > BTEAB > TBAC> TBAB.

Fig. 2. Dichlorocarbene addition to α- methyl styrene Dependence of k_{app} on [catalyst].



Effect of the amount of α- methyl styrene

Kinetic experiments were performed by varying the substrate amount ranging from 2.34 to 10.15 mmol of α-methyl styrene maintaining other experimental parameters such as chloroform and 30% NaOH in excess (Table 2). The k_{app} reaction rate increases with increase in the concentration of substrate. Generally, in pseudo first order reaction kinetics, the observed reaction rate is directly proportional to the amount of the organic substrate.

Table 1: Comparison of k_{app} with various single-site PTC's

Entry	PTC	Amount* (mol %)	k_{app} x10^{-3} (mol^{-1})
1	TBAB	0.1	3.12
2	TBAC	0.1	5.25
3	BTEAB	0.1	6.48
4	BTEAC	0.1	7.12

Table 2: Effect of variation of substrate amount

Substrate amount (mmol)	k_{app} x10^{-3} (mol^{-1})
2.34	10.8
3.90	9.51
5.46	8.36
7.03	7.12
8.59	5.20
10.5	3.21

Influence of alkali concentration.

The rate of dichlorocarbene addition strongly depends on the concentration of NaOH. The effect of varying (NaOH) on the rate of dichlorocarbene addition to α-methyl styrene was studied by varying sodium hydroxide concentration from 8.25 to 25.0 M keeping other parameters constant. The rate constants were found to increase with an increase in NaOH concentration. This may be attributed to the fact that hydroxide ions are less solvated by water molecules and thereby the activity of hydroxide ion increases. A plot –ln (1-X) verse time of the reaction rate constant against sodium hydroxide concentration gives a straight line (Fig. 3). Similar trend was observed by Rajendran *et al* (2007) and Landini *et al* (1986) on increasing NaOH concentration using onium salts. In the present study 30% NaOH is the optimum concentration required to get higher conversions. A lower amount of NaOH is particularly helpful for easy reaction work-up and durability of the reaction vessels.

Influence of temperature variation

On increasing the temperature from 30°C to 50°C, the rate of dichlorocyclopropanation of α-Methyl styrene also increases. The energy of activation is calculated from the Arrhenius plot, Ea = 16.07 kcal mol^{-1} (Fig. 4). The other thermodynamic parameters, i.e. $\Delta S^{\#}$, $\Delta G^{\#}$ and $\Delta H^{\#}$ were evaluated as -13.92 kcal mol^{-1}, 18.29 kcal mol^{-1} and 16.45 kcal mol^{-1} respectively. A higher Ea value has been reported (Tomoi and Ford, 1981) for the polystyrene bound triethylammoniumion catalyzed reaction, which was controlled by strictintrinsic reactivity under triphase reactions. In our case, the activation energy for the dichlorocarbene addition to α-methyl styrene is16.07 kcal molÿ1 and hence interfacial mechanism was proposed for the reaction study, which is governed by diffusion control.

Fig. 3. Dichlorocarbene addition to α- methyl styrene Dependence of k_{app} on NaOH.

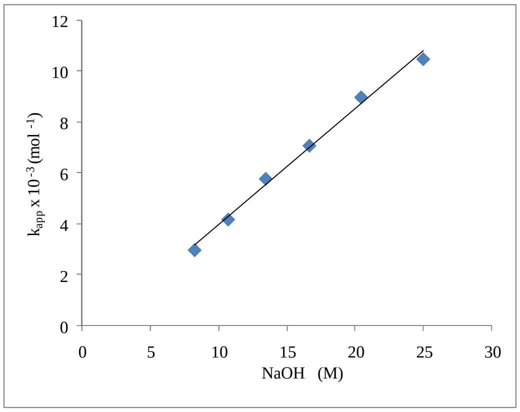
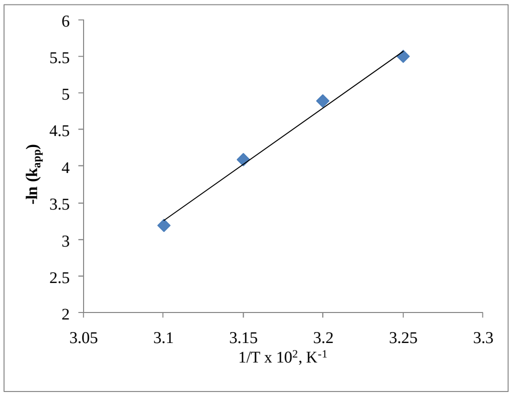
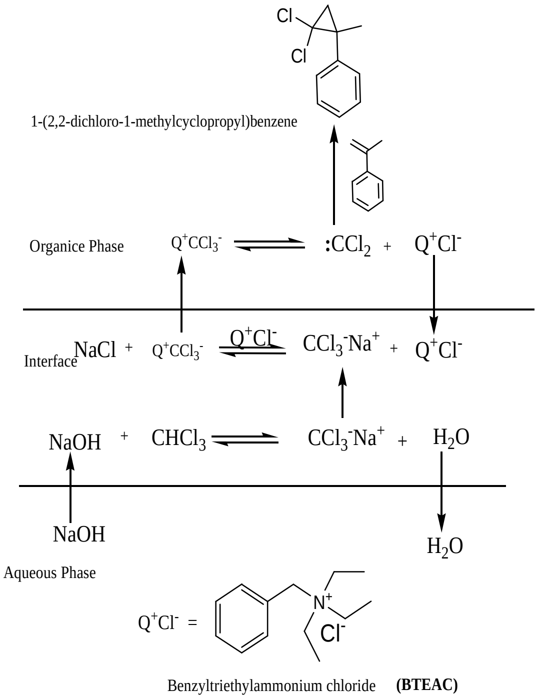


Fig. 4. Dichlorocarbene addition to α- methyl styrene Dependence of k_{app} on temperature.



Reaction mechanism

In general, mechanism of dihalocarbene addition reactions under PTC conditions are of classified into two types viz., (i) Stark's Extraction mechanism and (ii) Makosza's interfacial mechanism. In Stark's Extraction mechanism (Starks and Owens, 1973) the hydroxide ion may be extracted from an aqueous reservoir into an organic phase with the help of quaternary onium cations. However in Makosza interfacial mechanism (Makosza, and Bialecka, 1977; Chiellini *et al*., 1980) deprotonation of the organic substrate by the hydroxideion occurs at the interface and the resulting organic anion is ferried by the catalyst from the interface into the bulk organic phase for subsequent reaction. According to this mechanism, the slowest reaction is the addition of: CCl_2 to olefins, considering the other steps as fast equilibrium processes. In the current study, a fractional order with respect to the catalyst concentration suggests that step (Starks *et al.*, 1994) is not the sole rate determining one and that the chemical reaction in the organic phase is also ratedetermining (Scheme 3). The effect of other experimental parameters such as stirring speed, sodium hydroxide concentration and temperature over the observed rate of the reaction support the interfacial mechanism proposed by Makosza for PTC/OH^-Systems.



Conclusions

In summary, a phase transfer catalyst, was use its catalytic efficiency was investigated by following dichlorocyclopropanation of α-methyl styrene. The kinetic parameters such as stirring speed, substrate amount, catalyst amount, sodium hydroxide concentration and temperature were found to influence the rate constant (k_{app}) values remarkably. The Ea values and the thermodynamic parameters such as $\Delta S^\#$, $\Delta G^\#$ and $\Delta H^\#$ were evaluated for the dichlorocarbene addition to α-methyl styrene. From the experimental evidence, it is obvious that the reaction follows an interfacial reaction mechanism. This two-site phase transfer catalyst exhibits higher reactivity than the conventional BTEAC, BTEAB, TBAC and TBAB catalysts.

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