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Environmentally Friendly Epoxidation of Styrene to Styrene Oxide using Hydrogen Peroxide under Liquid-Liquid Phase Transfer Catalysis

Juvekar Ninad S.; Khandalkar Umakant W.; Mistry Cyrus K.*

Department of Chemical Engineering, Mahatma Gandhi Mission's College of Engineering and Technology, University of Mumbai, Kamothe, Navi Mumbai, Maharashtra,410209 India

***Corresponding Author cyruskmistry52@gmail.com**

Abstract : Phase transfer catalysis (PTC) is an attractive technique for synthesis of organic chemicals from two immiscible reactants existing in two different phases, which otherwise normally cannot react with each other due to their low mutual solubility in other phase and hence their low interaction. In this research work, an environmentally friendly catalytic epoxidation system is developed for the synthesis of styrene oxide from styrene using hydrogen peroxide as the oxidizing agent under liquid-liquid phase transfer catalytic conditions by using tetra-butyl ammonium bromide (TBAB) as the phase transfer catalyst and sodium tungstate as the co-catalyst. The use of co-catalyst with PTC has proven to be advantageous in intensifying the rate of oxidation reactions with H_2O_2. The kinetics of epoxidation of styrene to styrene oxide under liquid-liquid phase transfer catalysis was studied. Styrene was converted quantitatively to styrene oxide with about 75% conversion of styrene to styrene oxide in ethyl acetate as the solvent at 50°C. The reaction takes place to a significant extent in 30 minutes at 50°C and at a speed of agitation of 1200 rpm. Thermal decomposition of hydrogen peroxide may become significant at temperatures of 70°C and above, and also beyond 60°C, thermal oligomerisation of styrene sets in; hence, all the experiments were carried out at 50°C. An apparent activation energy of 2.5 kcal/gmol was found from the Arrhenius plot for the temperature range of 30°C-50°C. The effect of various parameters such as speed of agitation, temperature, concentration of styrene, concentration of H_2O_2, concentration of phase transfer catalyst such as TBAB and concentration of co-catalyst such as sodium tungstate on the conversion of styrene was studied. A suitable reaction mechanism and kinetic model for the above-mentioned environmentally friendly catalytic epoxidation system was also developed.

Key-words : Phase Transfer Catalysis; Styrene Oxide; Styrene; Hydrogen Peroxide; Environmentally Friendly Epoxidation; Kinetic Model.

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INTRODUCTION

The catalytic epoxidation of olefins has been a subject of growing interest in the production of chemicals and fine chemicals, since epoxides are key starting materials for a wide variety of products [1]. Styrene oxide is an important fine chemical intermediate used in the production of epoxy resins, cosmetics, surface coatings, plasticizers, anthelmintics, sweeteners, perfume, drugs, etc [2]. Styrene oxide is traditionally produced by the epoxidation of styrene using stoichiometric amounts of organic peracids as an oxidizing agent. However, peracids are very expensive, corrosive, hazardous to handle, non-selective for the epoxide formation and also lead to formation of undesirable products, creating a lot of waste [3]. Thus, environmentally friendly methods for epoxidation of styrene with clean oxidant have been a subject of current research. From the environmental and economic viewpoints, hydrogen peroxide is an ideal oxidant used for the epoxidation of olefin since it is relatively less expensive, easily available, environmentally safe and forms innocuous water as the only by-product [4, 5].

Recently, use of a number of solid catalysts such as Ti/SiO_2 [6], TS-1 [7], TBS-2 and TS-2 [8] and c-alumina [9] for the epoxidation of styrene by aqueous [6–9] or anhydrous [9] H_2O_2, H_2O_2-urea adduct [10] or TBHP [11, 12] has been reported. However, the use of these catalysts is limited because of their poor activity (low styrene conversion) [6–10] and/or poor selectivity [7, 8] for styrene oxide or deactivation by the reaction water [9]. Hence, it is of both scientific and practical importance to find a novel heterogeneous catalyst, which can be easily separated from the reaction mixture and also shows high activity and selectivity in the epoxidation of styrene [13].

Phase transfer catalysis (PTC) is an attractive technique for synthesis of organic chemicals from two immiscible reactants existing in two different phases, which otherwise normally cannot react with each other due to their low mutual solubility in other phase and hence their low interaction. Four of the many benefits of PTC include increasing yield, reducing excess reactants, conducting reactions under solvent free PTC conditions and dramatically reducing the reaction temperature [14, 15]. The use of co-catalysts with PTC has proven to be advantageous in intensifying the rates of oxidation reactions with H_2O_2. The tungstate complex serves as an excellent pre-catalyst because it does not cause unproductive decomposition of H_2O_2 [16, 17]. In this research work, it is proposed to use tetra butyl ammonium bromide (TBAB) as a phase transfer catalyst and sodium tungstate as a co-catalyst.

In the present work, an environmentally friendly catalytic epoxidation system is developed for the synthesis of styrene oxide from styrene using 30% aqueous hydrogen peroxide as the oxidizing agent under liquid-liquid phase transfer catalytic conditions by using tetra-butyl ammonium bromide (TBAB) as the phase transfer catalyst and sodium tungstate as the co-catalyst. The use of hydrogen peroxide (H_2O_2) as the oxidizing agent in the presence of PTC gives water as the only by-product which makes the reaction environmentally friendly.

EXPERIMENTAL SECTION

Materials

Styrene and Tetra Butyl Ammonium Bromide (TBAB) were obtained from M/s Research Lab Fine Chem Industries, Mumbai, India. Hydrogen Peroxide (H_2O_2 - 30% w/v Solution), Sodium tungstate ($Na_2WO_4.2H_2O$) and Ethyl Acetate were obtained from M/s SD Fine Chem Ltd., Mumbai, India.

Procedure

The experimental set-up consists of a batch reactor. The reactions are carried out batch-wise with necessary safety precautions, in a fully baffled mechanically agitated glass reactor of capacity 500 cm^3. A four-bladed glass disk turbine impeller located at a height of 1.5 cm from the bottom of the reactor with the provision of speed regulation is used for stirring the reaction mixture. The reactor is kept in a constant temperature water bath whose temperature can be controlled within ±1°C.

Typical procedure for liquid-liquid PTC reactions consisted of first preparing the aqueous phase and organic phase separately. The aqueous phase is prepared by taking required amount of 30 % w/v hydrogen peroxide solution ($1.76x10^{-3}$ gmol of H_2O_2) and then adding required amount of co-catalyst sodium tungstate ($4.4x10^{-5}$ gmol) to it and the reaction mixture is stirred until the co-catalyst sodium tungstate is completely dissolved in it. The total volume of the aqueous phase is made up to 200 cm^3 by adding distilled water to it. The organic phase is prepared by taking required amount of styrene ($1.76x10^{-3}$ gmol) and adding ethyl acetate as a solvent until the total volume of the organic phase becomes 200 cm^3. The aqueous phase and organic phase is then transferred to the 500 cm^3 glass reactor. The required amount of phase transfer catalyst (PTC) namely TBAB ($8.8x10^{-5}$ gmol) is then added to the reaction mixture and this two-phase mixture is stirred at the required speed of agitation (1200 rpm) at the required temperature (typically 50^0C) for the desired time period (30 mins).

The samples of the aqueous phase are collected in the sample bottles at regular intervals and were analysed for their hydrogen peroxide content by using iodometric titration. From the hydrogen peroxide content of the aqueous phase at the start of the reaction and the aqueous phase samples at various reactions times, the amount of hydrogen peroxide consumed in the reaction was calculated. The amount of hydrogen peroxide decomposed as a result of thermal decomposition at the reaction temperatures used was considered to be negligible for the short reaction times. Then the conversion of styrene was calculated by stoichiometry from the amount of hydrogen peroxide consumed in the reaction.

DEVELOPMENT OF REACTION MECHANISM AND KINETIC MODEL

Reaction Mechanism

The following steps are assumed to take place in the liquid-liquid phase transfer catalyzed (L-L PTC) epoxidation of styrene to styrene oxide using hydrogen peroxide as the oxidizing agent and sodium tungstate as the co-catalyst.

Step 1:

Formation of bisperoxotungstate compound $Na_2[WO(O_2)_2(OH)_2]$ in the aqueous phase from sodium tungstate and hydrogen peroxide:

$$Na_2WO_4 + 2H_2O_2 \longrightarrow Na_2\,[WO(O_2)_2(OH)_2] + H_2O$$

Step 2:

Formation of the mono-protonated form of the bisperoxotungstate compound in the aqueous phase:

$$Na_2[WO(O_2)_2(OH)_2] + H^+ \rightleftharpoons Na^+[WO(O_2)_2(OH)(H_2O)]^- + Na^+$$

Step 3:

Dissociation of the phase transfer catalyst (Tetrabutyl Ammonium Bromide, TBAB) in the aqueous phase:

$$\{Q^+Br^-\}_{aq} \rightleftharpoons Q^+ + Br^-$$

where the quaternary ammonium ion pairs are shown in { }.

It is to be noted that the phase transfer catalyst (TBAB) initially added to the organic phase gets partitioned into both the aqueous phase and organic phase.

Step 4:

Formation of the quaternary ammonium ion pair $\{Q^+[WO(O_2)_2(OH)(H_2O)]^-\}$ in the aqueous phase by Na^+-Q^+ ion exchange:

$$Q^+ + Na^+[WO(O_2)_2(OH)(H_2O)]^- \rightleftharpoons \{Q^+[WO(O_2)_2(OH)(H_2O)]^-\}_{aq} + Na^+$$

Step 5:

Transfer of the quaternary ammonium ion pair $\{Q^+[WO(O_2)_2(OH)(H_2O)]^-\}$ from the aqueous phase to the organic phase interface :

$$\{Q^+[WO(O_2)_2(OH)(H_2O)]^-\}_{aq} \rightleftharpoons \{Q^+[WO(O_2)_2(OH)(H_2O)]^-\}_{org,i}$$

where the subscripts aq and org denote the aqueous phase and organic phase, respectively, and the subscript i denotes the interface.

Step 6:

Transfer of the quaternary ammonium ion pair $\{Q^+[WO(O_2)_2(OH)(H_2O)]^-\}$ from the organic phase interface to the bulk organic phase :

$\{Q^+[WO(O_2)_2(OH)(H_2O)]^-\}_{org,i} \rightleftharpoons \{Q^+[WO(O_2)_2(OH)(H_2O)]^-\}_{org,b}$

where the subscript org denotes the organic phase, and the subscripts i and b denote the interface and bulk phase, respectively.

Step 7:

Reaction between the quaternary ammonium ion pair $\{Q^+[WO(O_2)_2(OH)(H_2O)]^-\}$ and styrene in the organic phase:

$\{Q^+[WO(O_2)_2(OH)(H_2O)]^-\}_{org} + C_8H_8 \longrightarrow C_8H_8O + \{Q^+[WOO(O_2)(OH)(H_2O)]^-\}_{org}$

Step 8:

Transfer of the quaternary ammonium pair $\{Q^+[WOO(O_2)(OH)(H_2O)]^-\}$ from the organic phase to the aqueous phase:

$\{Q^+[WOO(O_2)(OH)(H_2O)]^-\}_{org} \rightleftharpoons \{Q^+[WOO(O_2)(OH)(H_2O)]^-\}_{aq}$

Step 9:

Formation of the monoperoxotungstate compound $Na^+[WOO(O_2)(OH)(H_2O)]^-$ in the aqueous phase by Na^+-Q^+ ion exchange:

$\{Q^+[WOO(O_2)(OH)(H_2O)]^-\}_{aq} + Na^+ \rightleftharpoons Na^+[WOO(O_2)(OH)(H_2O)]^- + Q^+$

Step 10:

Oxidation of the monoperoxotungstate compound $Na^+[WOO(O_2)(OH)(H_2O)]^-$ in the aqueous phase by hydrogen peroxide:

$Na^+[WOO(O_2)(OH)(H_2O)]^- + H_2O_2 \rightleftharpoons Na^+[WO(O_2)_2(OH)(H_2O)]^- + H_2O$

The oxidation of the monoperoxotungstate ion to the bisperoxotungstate ion may also occur at the organic-aqueous interface or even in the organic phase to some extent.

Kinetic Model (Theoretical or Mathematical Model)

Based on the experimental results obtained a kinetic model (mathematical model) has been proposed for the given reaction system. It is assumed in the present case that steps 1, 2, 3, 4, 5, 7, 8, 9, 10 and 11 are fast compared to step 6 which is the slowest step and hence the rate controlling step.

At steady state, the following rate equation may be written for step 6 of the proposed theoretical model:

$r = -d[C_8H_8]/dt$

$= R_c\underline{a} = k_{LC}\underline{a}([Q^+[WO(O_2)_2(OH)(H_2O)]^-]_{org,i} - [Q^+[WO(O_2)_2(OH)(H_2O)]^-]_{org,b})$ (Equation 1)

where r denotes the intrinsic rate of chemical reaction of styrene to styrene oxide in the organic phase,

$R_c\underline{a}$ = Volumetric rate of transfer of $\{Q^+[WO(O_2)_2(OH)(H_2O)]^-\}$ from the interface to the bulk organic phase,

$k_{LC}\underline{a}$ = Mass transfer coefficient for transfer of $\{Q^+[WO(O_2)_2(OH)(H_2O)]^-\}$ from the interface to the bulk organic phase,

$\underline{a}$ = Interfacial area per unit volume of the organic phase.

The subscripts i and b indicate the interface and bulk concentrations, respectively.

If the reaction system conforms to the Slow Reaction Regime (Regime 2), then there will be no free $\{Q^+[WO(O_2)_2(OH)(H_2O)]^-\}$ present in the bulk organic phase i.e. $[Q^+[WO(O_2)_2(OH)(H_2O)]^-]_{org.,b} = 0$ and the following rate equation will be valid:

$R_c\underline{a} = k_{LC}\underline{a}\,[Q^+[WO(O_2)_2(OH)(H_2O)]^-]_{org,I}$ (Equation 2)

The rate of reaction is independent of the concentration of styrene and thus the reaction is zero-order with respect to the concentration of styrene.

Let $[Q_t]$ be the total catalyst concentration per organic phase volume then the following equation for $[Q_t]$ can be written as:

$[Q_t] = [Q^+[WO(O_2)_2(OH)(H_2O)]^-]_{org} + [Q^+[WOO(O_2)(OH)(H_2O)]^-]_{org} + ([Q^+[WO(O_2)_2(OH)(H_2O)^-]]_{aq} + [Q^+[WOO(O_2)(OH)(H_2O)]^-]_{aq} + [Q^+]_{aq})\ V_{aq}/V_{org}$ (Equation 3)

Let AS denote the active peroxo species or active oxidizing species namely $[WO(O_2)_2(OH)(H_2O)]^-$ and SPS denote the subsequent peroxo species $[WOO(O_2)(OH)(H_2O)]^-$

The following equilibrium relationships are valid:

$K_1 = [Q^+[AS]^-]_{org} / [Q^+[AS]^-]_{aq}$ (Equation 4)

$K_2 = [Q^+[SPS]^-]_{org} / [Q^+[SPS]^-]_{aq}$ (Equation 5)

Therefore, we can write:

$[Q^+[AS]^-]_{aq} = [Q^+[AS]^-]_{org} / K_1$ (Equation 6)

$[Q^+[SPS]^-]_{aq} = [Q^+[SPS]^-]_{org} / K_2$ (Equation 7)

Substituting the values of $[Q^+[AS]^-]_{aq}$ and $[Q^+[SPS]^-]_{aq}$ from equations 6 and 7 in equation 3 gives:

$[Q_t] = [Q^+[AS]^-]_{org} + [Q^+[SPS]^-]_{org} + (([Q^+[AS]^-]_{org} /K_1) + ([Q^+[SPS]^-]_{org}/K_2) + [Q^+]_{aq})V_{aq}/\ V_{org}$ (Equation 8)

Since the mole ratio of the oxidizing agent i.e. hydrogen peroxide (H_2O_2) to the phase transfer catalyst (TBAB) is large it may be assumed that the concentration of free quaternary ammonium cation in the aqueous phase, $[Q^+]_{aq}$ is very small and may be neglected.

Therefore, Equation 8 may be written as:

$[Q_t]= ((1+(1/K_1)(V_{aq}/V_{org}))[Q^+[AS^-]]_{org} + ((1+(1/K_2)(V_{aq}/V_{org}))[Q^+[SPS^-]]_{org}$ (Equation 9)

Since the transfer of $\{Q^+[SPS]^-\}$ ion pair from the organic phase to the aqueous phase is assumed to be very fast, the concentration of $\{Q^+[SPS]^-\}$ ion pair in the organic phase may be considered to be negligible i.e.;

$[Q^+[SPS]^-]_{org} = 0$

Therefore Equation 8 may be written as:

$[Q_t] = ((1+(1/K_1)(V_{aq}/V_{org}))[Q^+[AS^-]]_{org}$ (Equation 10)

Now, let $V_r = V_{org} /V_{aq}$ = organic phase to aqueous phase volume ratio

$[Q_t] = ((1+(1/K_1)(1/V_r))[Q^+[AS]^-]_{org}$ (Equation 11)

$[Q_t] = ((K_1V_r+1)/K_1Vr)[Q^+[AS]^-]_{org}$ (Equation 12)

$[Q^+[AS]^-]_{org} =((K_1V_r/(K_1V_r+1))[Q_t]$ (Equation 13)

$[Q^+[AS]^-]_{org} = \varphi\ [Q_t]$ (Equation 14)

where $\varphi = K_1V_r / (K_1V_r +1)$

Substituting the value of $[Q^+[AS]^-]_{org}$ from Equation 14 in Equation 2 gives:

$R_c\underline{a} = k_{LC}\underline{a}\ \varphi\ [Q_t]$ (Equation 15)

The above Equation 15 suggests that the reaction is first-order with respect to the total concentration of the phase transfer catalyst in the organic phase.

Now, from Equation 4:

$[Q^+[AS]^-]_{org} = K_1\ [Q^+[AS]^-]_{aq}$ (Equation 16)

Substituting the value of $[Q^+[AS]^-]_{org}$ from Equation 16 in Equation 12 gives:

$[Q_t] = ((K_1V_r+1)/K_1V_r)K_1[Q^+[AS]^-]_{aq}$ (Equation 17)

$[Q_t] = (K_1/\varphi)\ [Q^+[AS]^-]_{aq}$ (Equation 18)

From Equation 18 it is observed that $[Q_t]$ varies linearly with $[Q^+[AS]^-]_{aq}$ and from Equation 15 it is observed that the rate of reaction r varies linearly with $[Q_t]$, therefore it may be concluded that r varies linearly with $[Q^+[AS]^-]_{aq}$ which is proportional to the concentration of sodium tungstate ($Na_2WO_4.2H_2O$) in the aqueous phase and concentration of hydrogen peroxide in the aqueous phase and thus the reaction should be first order with respect to the concentration of sodium tungstate ($Na_2WO_4.2H_2O$) in the aqueous phase and concentration of hydrogen peroxide in the aqueous phase.

RESULTS AND DISCUSSION

The validity of the proposed kinetic (theoretical) model was tested against the experimental data obtained during the study of effect of various reaction parameters and are described in the following sections. Preliminary experiments showed that there was no significant reaction in the absence of a phase transfer catalyst, viz. TBAB and the co-catalyst, viz. sodium tungstate.

Effect of Speed of Agitation

To ascertain the influence of mass transfer limitations in the L-L PTC epoxidation of styrene with H_2O_2, the speed of agitation was varied in the range of 300-1200 rpm under otherwise similar conditions (namely, 0.352 gmol of styrene in 200 cm^3 organic phase, 0.352 gmol of H_2O_2 in 200 cm^3 aqueous phase, 8.8×10^{-5} gmol/cm^3 of PTC (TBAB), 4.4×10^{-5} gmol/cm^3 of sodium tungstate, temperature = 50°C) as shown in Fig. 1. The conversion of styrene was found to increase when the speed of agitation was increased from 300 to 1200 rpm. This suggests that mass transfer effects are significant in this oxidation reaction. The effect of speed of agitation on the initial rate of reaction was studied and it was found that the initial rate of reaction was found to be dependent on the speed of agitation as shown in Fig. 2. This shows that there is mass transfer limitation in this oxidation reaction. Thus, the experimental results obtained indicate that mass transfer effects are significant in the oxidation reaction.

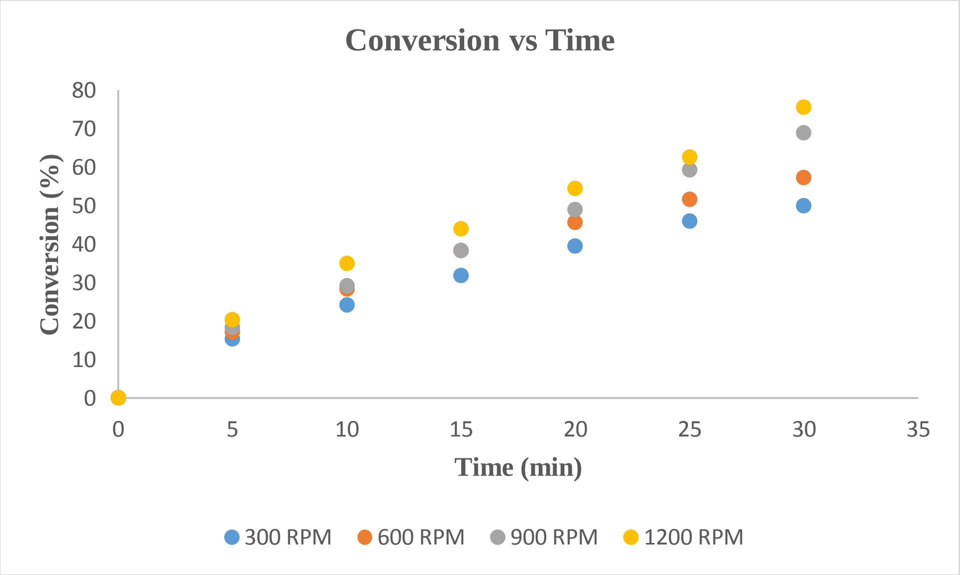

Fig. 1: Effect of Speed of Agitation on Conversion of Styrene

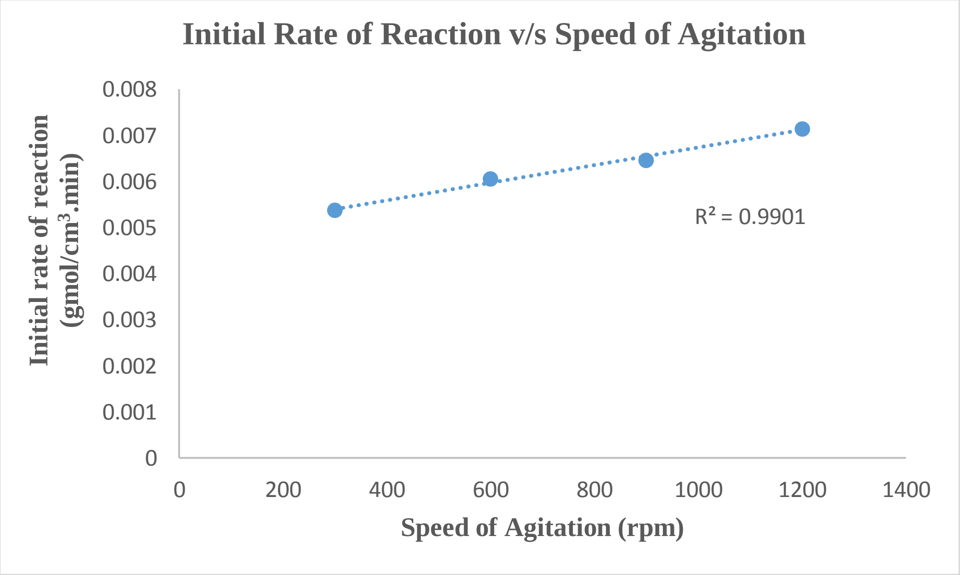

Fig. 2: Initial Rate of Reaction v/s Speed of Agitation

Effect of Temperature

The effect of temperature on the oxidation of styrene was studied by varying the temperature from 30˚C (303K) to 50˚C (323K) under otherwise similar conditions (namely, 0.352 gmol of styrene in 200 cm^3 organic phase, 0.352 gmol of H_2O_2 in 200 cm^3 aqueous phase, 8.8x10^{-5} gmol/cm^3 of PTC (TBAB), 4.4x10^{-5} gmol/cm^3 of sodium tungstate, speed of agitation = 1200 rpm) as shown in Fig. 3. The conversion of styrene was observed to increase with increase in reaction temperature. Thermal decomposition of hydrogen peroxide may become significant at temperatures of 70˚C and above, and also beyond 60°C, thermal oligomerisation of styrene sets in; hence, all the experiments were carried out at 50°C. The calculated activation energy from the Arrhenius plot for the temperature range of 30˚C-50˚C is 2.5 kcal/gmol (Fig. 4), which indicates that mass transfer effects are significant and the reaction is not kinetically controlled.

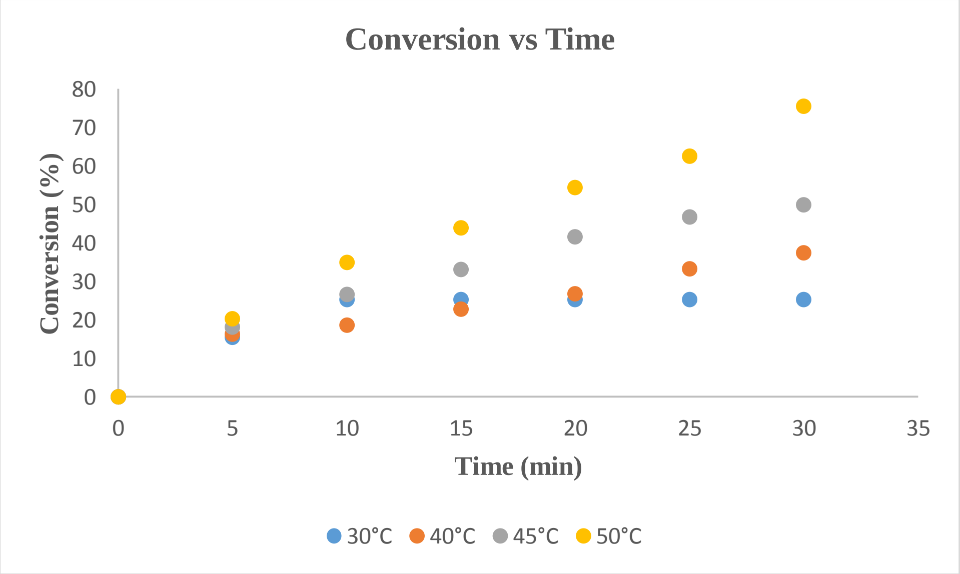

Fig. 3: Effect of Temperature on Conversion of Styrene

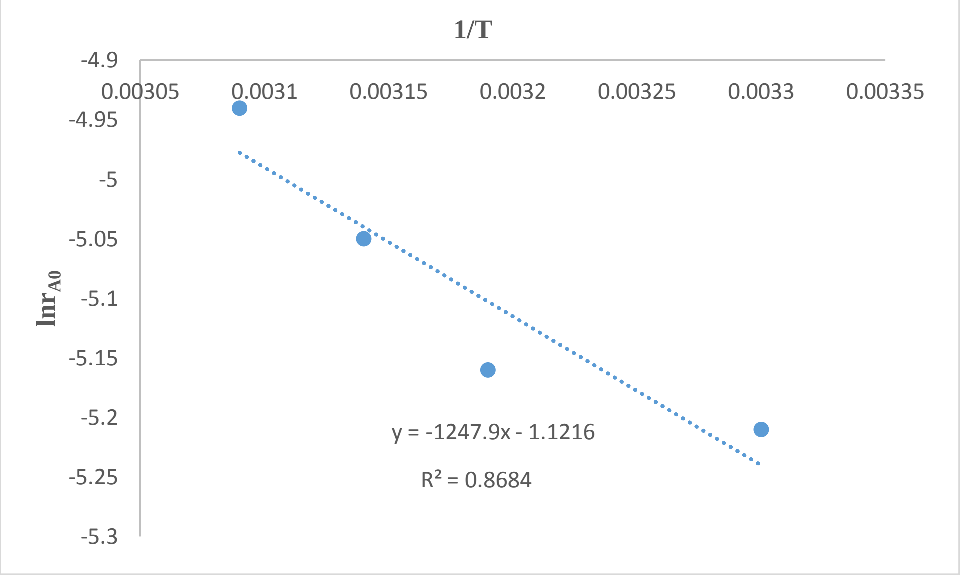

Fig. 4: Arrhenius Plot

Effect of Concentration of Styrene

The effect of concentration of styrene was studied by varying its concentration in the organic phase from 0.00176 gmol/cm^3 to 0.0044 gmol/cm^3 under otherwise similar conditions (namely, 0.352 gmol of H_2O_2 in 200 cm^3 aqueous phase, 8.8x10^{-5} gmol/cm^3 of PTC (TBAB), 4.4x10^{-5} gmol/cm^3 of sodium tungstate, temperature = 50°C, speed of agitation = 1200 rpm). It is observed that conversion of styrene increases with increase in concentration of styrene as shown in Fig. 5. The plot of initial rate of reaction versus concentration of styrene is shown in Fig. 6. The initial rate of reaction remains approximately constant with increase in concentration of styrene. The plot of initial rate of reaction versus concentration of styrene is a horizontal line which suggests that it is a zero-order reaction with respect to the concentration of styrene.

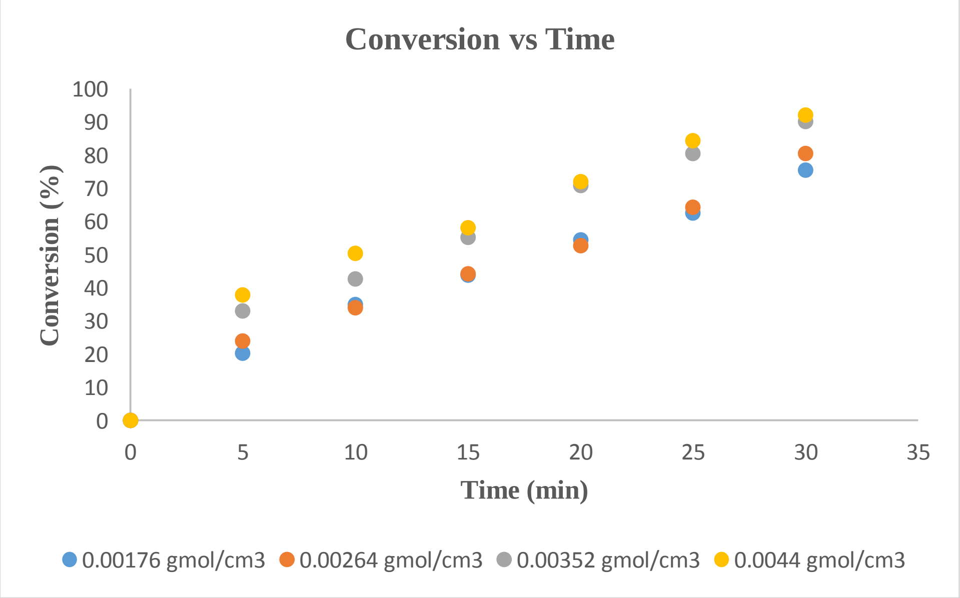

Fig. 5: Effect of Concentration of Styrene

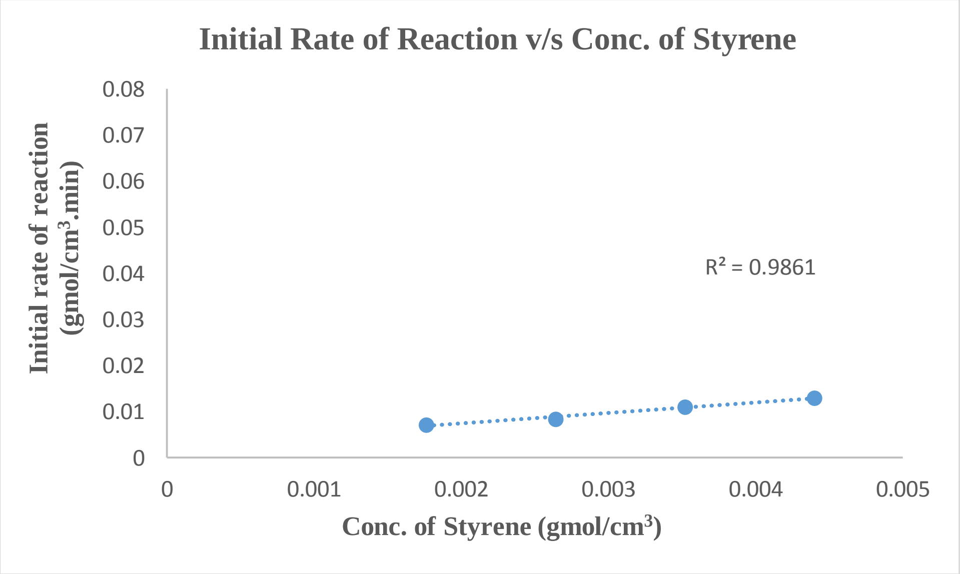

Fig. 6: Initial Rate of Reaction v/s Concentration of Styrene

Effect of Concentration of Hydrogen Peroxide

The effect of concentration of hydrogen peroxide on the conversion of styrene was studied as shown in Fig. 7. The concentration of hydrogen peroxide was varied from 0.00044 gmol/cm^3 to 0.00176 gmol/cm^3 in the aqueous phase under otherwise similar conditions (namely, 0.352 gmol of styrene in 200 cm^3 organic phase, 8.8x10^{-5} gmol/cm^3 of PTC (TBAB), 4.4x10^{-5} gmol/cm^3 of sodium tungstate, temperature = 50°C, speed of agitation = 1200 rpm). It is observed that the conversion of styrene in the organic phase increases as the concentration of hydrogen peroxide in the aqueous phase decreases. The plot of initial rate of reaction versus concentration of hydrogen peroxide is shown in Fig. 8. It is observed that the initial rate of reaction increases linearly with the concentration of hydrogen peroxide in aqueous phase which indicates that the reaction is first-order with respect to the concentration of hydrogen peroxide in the aqueous phase.

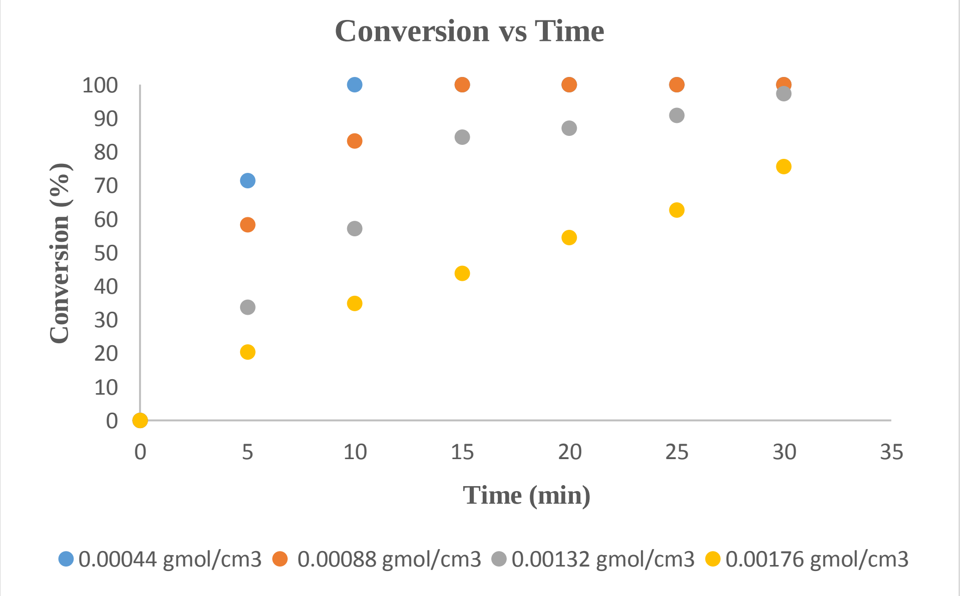

Fig. 7: Effect of Concentration of Hydrogen Peroxide

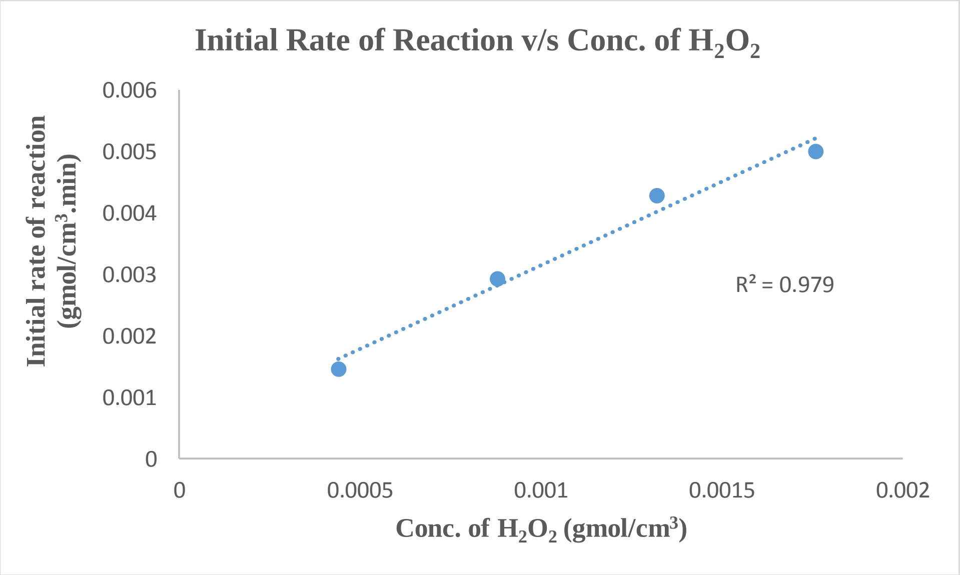

Fig. 8: Initial Rate of Reaction v/s Concentration of Hydrogen Peroxide

Effect of Phase Transfer Catalyst Concentration

The effect of phase transfer catalyst (tetra butyl ammonium bromide, TBAB) concentration on the conversion of styrene was studied as shown in Fig. 9. The concentration of PTC was varied from 8.8x10^{-5} gmol/cm^3 to 1.4x10^{-4} gmol/cm^3 under otherwise similar conditions (namely, 0.352 gmol of styrene in 200 cm^3 organic phase, 0.352 gmol of H_2O_2 in 200 cm^3 aqueous phase, 4.4x10^{-5} gmol/cm^3 of sodium tungstate, temperature = 50°C, speed of agitation = 1200 rpm). It is observed that the conversion of styrene increases with increase in concentration of the phase transfer catalyst. The plot of initial rate of reaction versus the concentration of phase transfer catalyst is shown in Fig. 10. As the concentration of PTC increases the initial rate of reaction also increases. It is observed from this plot that the initial rate of reaction increases linearly with the concentration of phase transfer catalyst which indicates that the reaction is first-order with respect to the concentration of phase transfer catalyst in the organic phase.

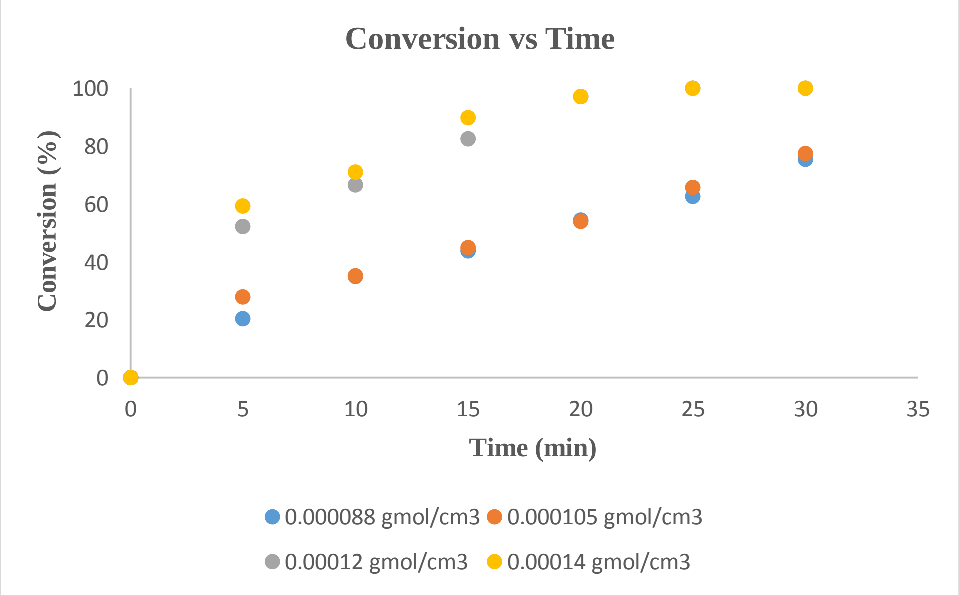

Fig. 9: Effect of Concentration of PTC

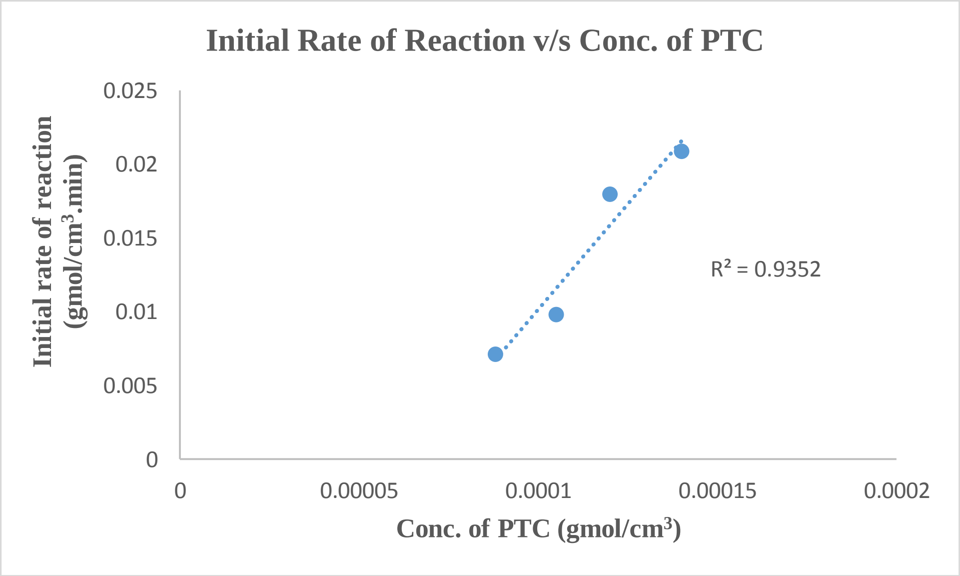

Fig. 10: Initial Rate of Reaction v/s Concentration of PTC

Effect of Co-catalyst Concentration

The effect of co-catalyst (sodium tungstate, $Na_2WO_4.2H_2O$) concentration on the conversion of styrene was studied as shown in Fig. 11. The concentration of co-catalyst was varied from 1.095×10^{-5} gmol/cm^3 to 4.4×10^{-5} gmol/cm^3 under otherwise similar conditions (namely, 0.352 gmol of styrene in 200 cm^3 organic phase, 0.352 gmol of H_2O_2 in 200 cm^3 aqueous phase, 8.8×10^{-5} gmol/cm^3 of PTC (TBAB), temperature = 50°C, speed of agitation = 1200 rpm). It is observed that the conversion of styrene increases with increase in concentration of the co-catalyst. The plot of initial rate of reaction versus concentration of co-catalyst is shown in Fig. 12. It is observed that the initial rate of reaction increases linearly with the concentration of co-catalyst which suggests that the reaction is first-order with respect to the concentration of the co-catalyst. It is also observed from this plot that the reaction may also take place to some extent even in the absence of a co-catalyst.

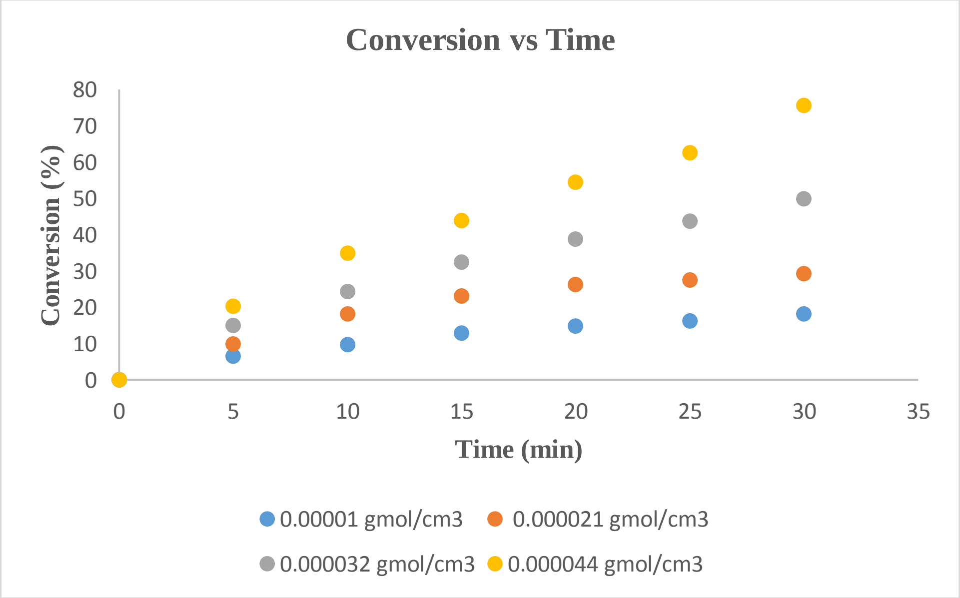

Fig. 11: Effect of Concentration of Co-catalyst ($Na_2WO_4.2H_2O$)

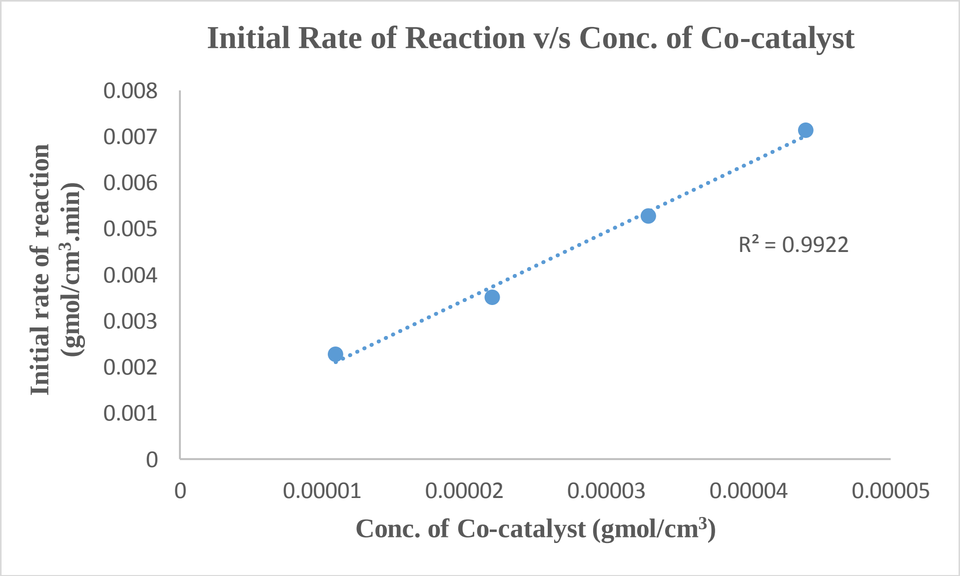

Fig. 12: Initial Rate of Reaction v/s Concentration of Co-catalyst

The above mentioned results are in agreement with the proposed kinetic model for this reaction system.

CONCLUSION

The epoxidation of styrene to styrene oxide was successfully carried out with hydrogen peroxide as an oxidizing agent under liquid-liquid phase transfer catalysis with tetra-butyl ammonium bromide (TBAB) as the phase transfer catalyst and sodium tungstate as the co-catalyst. The effect of speed of agitation, temperature, concentration of styrene in the organic phase, concentration of hydrogen peroxide (H_2O_2) in the aqueous phase, concentration of phase transfer catalyst (TBAB) in the organic phase and concentration of sodium tungstate ($Na_2WO_4.2H_2O$) in the aqueous phase on the initial rate of reaction was investigated as well as the conversion of styrene versus time profiles for the effect of each of these reaction parameters were plotted. It was observed that the conversion of styrene increases with temperature, speed of agitation, concentration of styrene in the organic phase, phase transfer catalyst concentration and co-catalyst concentration.

The reaction may be considered to be mass transfer controlled at a speed of agitation of 300 to 1200 rpm. The value of the activation energy of 2.5 kcal/gmol obtained from the Arrhenius plot indicates that mass transfer limitations are significant and suggests that the reaction is not kinetically controlled.

The study of the effect of concentration of styrene in the organic phase suggests that the reaction is zero order with respect to the concentration of styrene. The study of the effect of concentration of hydrogen peroxide in the aqueous phase suggests that the reaction is first order with respect to the concentration of hydrogen peroxide.

The initial rate of reaction was found to vary linearly with the concentration of the phase transfer catalyst in the organic phase which suggests that the reaction is first order with respect to the concentration of the phase transfer catalyst. The initial rate of reaction was found to vary linearly with the concentration of the co-catalyst in the aqueous phase which suggests that the reaction is first order with respect to the concentration of the co-catalyst.

A suitable reaction mechanism and a kinetic model have been proposed to explain the experimental results obtained as a part of this research work.

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