

Kinetics of Environmentally Friendly Phase Transfer Catalytic Oxidation of 4-Methoxybenzyl Alcohol to 4-Methoxybenzaldehyde with Hydrogen Peroxide

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Abstract

The environmentally friendly oxidation using phase transfer catalysis involves the migration of a reactant in a heterogeneous system from one phase into another phase to make the reaction possible. Addition of a phase transfer catalyst enhances the rate of transfer of water-soluble reactant across the interface to the organic phase. In this article an environmentally friendly catalytic oxidation system for the synthesis of 4-methoxybenzaldehyde from 4-methoxy benzyl alcohol using hydrogen peroxide as the oxidizing agent under phase transfer catalytic conditions with sodium tungstate as a co-catalyst has been reported. Applications of environmentally friendly oxidation reactions using hydrogen peroxide are diverse, ranging from pulp and textile bleaching to production of fine chemicals. The effect of various parameters such as speed of agitation, temperature, concentration of 4-methoxybenzyl alcohol, concentration of H₂O₂, phase transfer catalyst loading and co-catalyst loading on the conversion of 4-methoxybenzaldehyde was studied. The kinetics of the environmentally friendly oxidation reaction under a liquid-liquid phase transfer catalysis was investigated. The phase transfer catalyst used was tetra butyl ammonium bromide (TBAB) and sodium tungstate was used as a co-catalyst. A kinetic model was also developed for the above-mentioned system.

Keywords- *Heterogeneous Catalysis, Environmentally Friendly Oxidation, Selective Oxidation, 4-methoxybenzaldehyde, Phase Transfer Catalysis, Kinetic Model.*

1. Introduction

Oxidation is a core technology for converting petroleum-based materials to useful chemicals of a higher oxidation state. However, oxidation is among the most problematic processes. Many textbook oxidation methods are unacceptable for practical synthesis; the heavy metal oxidants form toxic wastes, while known organic stoichiometric oxidants are usually very expensive. Nitric acid, the most conventional industrial oxidant, is cheap but unavoidably forms various nitrogen oxides. Thus, there is a need for the invention of clean, safe oxidation procedures. H₂O₂ is a very attractive oxidant. It can easily oxidize organic compounds since it contains 47% active oxygen and results in the generation of water as the only by-product. It is relatively inexpensive. Aqueous H₂O₂ is an ideal oxidant, when coupled with a tungstate complex and a quaternary ammonium ion as a phase-transfer catalyst. The phase transfer mechanism proposed by Starks accounts for the major features of the reaction (Starks, 1971; Starks et al., 1994). Liquid phase catalytic oxidation of alcohols is a fascinating reaction and is one of the most important synthetic reactions in organic chemistry (Nayori et al., 2003). 4-methoxybenzaldehyde is commonly encountered in fragrances, both synthetic and natural. It is widely used in flavoring industry and as an intermediate in the synthesis of other compounds important in the pharmaceutical and perfumery industry. A solution of 4-methoxybenzaldehyde in

acid and ethanol is a useful stain in thin layer chromatography. The oxidation of 4-methoxybenzyl alcohol to 4-methoxybenzaldehyde has been accomplished by the use of a wide variety of reagents or catalysts and different reaction procedures. Several reagents have been used for this transformation such as nitric acid, thallium nitrate, copper sulfate, copper acetate, ammonium nitrate and bismuth oxide. The conventional oxidizing agents are permanganate, dichromate or chromic acid, manganese dioxide and manganese acetate.

In this research work the selective oxidation of 4-methoxybenzyl alcohol to 4-methoxybenzaldehyde was studied under liquid-liquid phase transfer conditions using hydrogen peroxide as the oxidizing agent with tetrabutyl ammonium bromide (TBAB) as the phase transfer catalyst and sodium tungstate as the co-catalyst. Organic solvent used in this oxidation reaction is ethyl acetate, and hydrogen peroxide is used as a clean oxidizing agent which produces water as the only by-product and makes the reaction environmentally friendly.

2. Material

4-methoxybenzyl alcohol was obtained from Neemco Chemicals Pvt. Ltd and hydrogen peroxide (H₂O₂- 30% w/v) was obtained from M/s Merck Specialties Pvt. Ltd., Mumbai, India. Sodium Tungstate (Na₂WO₄·2H₂O) and Tetrabutyl Ammonium Bromide (TBAB) of 99.5% purity were obtained from M/s Merck Specialties Pvt. Ltd., Mumbai.

3. 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 cm³. A four-bladed glass disk turbine impeller 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 liquid-liquid PTC reactions were conducted by taking 30 % w/v hydrogen peroxide solution (0.1 gmol of H₂O₂) adding sodium tungstate (0.0005 gmol) and the total volume of the aqueous phase was made up 50 cm³(using a 100 cm³ standardization volumetric flask) by adding distilled water to it. Then the required amount of 4-methoxybenzyl alcohol (0.1 gmol) which forms the

organic phase is added to the 50 cm³ aqueous phase. Then the whole solution was added to the 500 cm³ glass reactor. The required amount of phase transfer catalyst (PTC) namely TBAB (0.001 gmol) was then added to the reaction mixture and this mixture was stirred at the required speed of agitation at the required temperature (60 °C) for the desired time period.

4. Discussion

4.1. Mechanism of reaction and kinetic model

Reaction mechanisms and kinetic models for phase transfer catalytic reactions have been proposed by many researchers (Do and Chou, 1990; Dehmlow and Dehmlow, 1993; Asai et al., 1994; Yadav and Mistry, 2001; Ranveer, 2011; More, 2012).

The mechanism shown in Fig.1 explains a range of experimental findings in the oxidation of alcohols including 4-methoxybenzyl alcohol. In an aqueous phase, the catalyst precursor Na₂WO₄ is rapidly oxidized by H₂O₂ according to the reaction: Na₂WO₄ + 2H₂O₂ → Na₂[WO(O₂)₂(OH)₂] + H₂O. The resulting bisperoxotungstate compound A is in equilibrium with B and C. The dianion in A is feebly active toward alcohols, while the mono- and di-protonated forms in B and C are sufficiently reactive. Therefore, the catalytic activity is highly dependent on the acidity of the reaction medium as well as the efficiency of aqueous-organic phase transfer of the active species aided by Q⁺. In a pH range above 4, the catalytic system that contains largely A has only weak oxidative activity even in the presence of Q⁺. Since the pK_a value of C is 0.1, the mono-protonated species B is dominant under reaction conditions with a pH range of 0.4–3, where the HSO₄⁻ ion is largely deprotonated to SO₄²⁻. Under such dilute conditions, B exists mostly as a monomer. Its anion moiety can easily be transferred to an organic phase by Na⁺-Q⁻ ion exchange. Thus, in the organic layer, the bisperoxo complex D undergoes water-alcohol ligand exchange to form E. Then proton transfer in E generates the reactive species F, which forms an aldehyde product (such as 4-methoxybenzaldehyde) and G (Nayori et al., 2003).

The alkoxy ligand in F is dehydrogenated by the adjacent hydroperoxy ligand via a six-membered transition state where the hydridic α-hydrogen migrates to the positively polarized oxygen atom. The monoperoxo tungstate ion in G is reoxidized by H₂O₂ after returning to the aqueous phase as the ion pair H. This step may also occur at an organic-aqueous interface or even in the organic

phase to some extent. The neutral bisperoxo compound C, present as a minor component, is reactive in a homogeneous phase but unable to move into the organic phase under the biphasic conditions. H₂WO₄, a Na⁺- free compound, acts as an excellent precatalyst but only with a PTC because of the operation of the same mechanism in the biphasic system (Nayori et al., 2003).

$$r = -d[C_8H_{10}O_2]/dt = k[Q^+[WO(O_2)_2(OH)(H_2O)]^-]_{org} [C_8H_{10}O_2]_{org}$$

(Equation 1)

where r denotes the intrinsic rate of chemical reaction of 4-methoxybenzyl alcohol to 4-methoxybenzaldehyde in the organic phase.

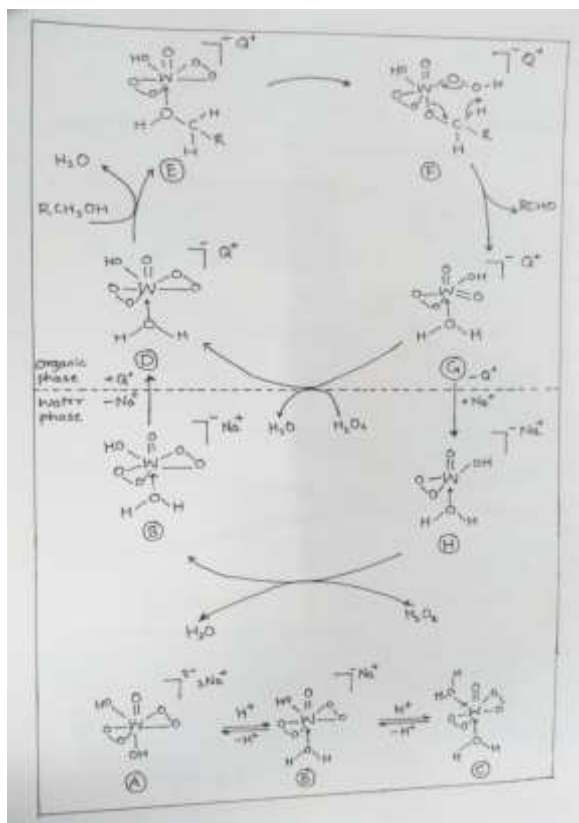
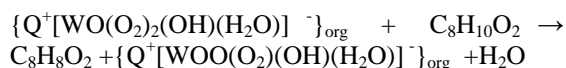


Fig. 1: Catalytic Cycle of Alcohol Oxidation using PTC-H₂O₂-Na₂WO₄.2H₂O system.

Based on the above mechanism, reaction between the quaternary ammonium pair {Q⁺[WO(O₂)₂(OH)(H₂O)]⁻} and 4-methoxybenzyl alcohol in the organic phase is:



where the subscript org denotes the organic phase.

While developing a kinetic model for this reaction system it has been assumed that the rate limiting step is the chemical reaction in the organic phase.

At steady state, the following rate equation may be written for this reaction rate controlling step:

4.2. Effect of different parameters

To validate the proposed mechanism, the effects of various parameters on rate of reaction were studied and are described in the following sections

4.2.1. Effect of speed of agitation

The effect of speed of agitation was studied by varying the speed of agitation from 300 rpm to 1500 rpm under otherwise similar conditions. As the speed of agitation increases from 300 rpm to 1500 rpm, the conversion of 4-methoxy benzyl alcohol increases as shown in Figure 2. It was observed that at low speeds of agitation, there is a mass transfer limitation in the liquid-liquid benzyl alcohol using hydrogen peroxide as an oxidizing agent. After 1500 rpm the conversion of 4-methoxy benzyl alcohol is constant so it can be concluded that it is the intrinsic rate of chemical reaction which is controlling the reaction at higher speeds of agitation. The initial rate of reaction is found to be dependent on the speed of agitation upto 1500 rpm as shown in the Figure 3.

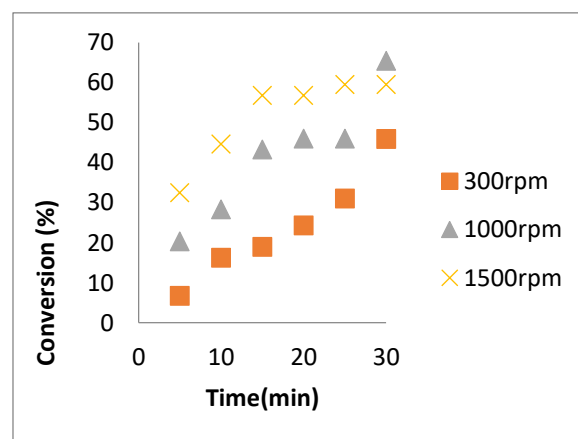


Fig. 2: Effect of Speed of Agitation on Oxidation on 4-methoxybenzyl alcohol

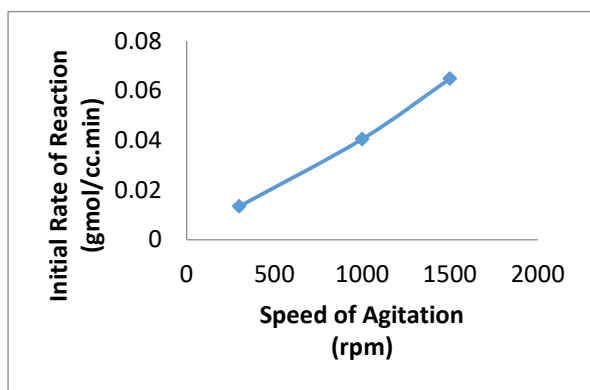


Fig. 3 : Initial Rate of Reaction V/s Speed of Agitation

4.2.2. Effect of temperature

The effect of temperature on the conversion of 4-methoxy benzyl alcohol was studied as shown in Figure 4. Experiments at various temperatures were carried out by varying the temperature from 30°C to 60°C under otherwise similar conditions (0.088 gmol of 4-methoxy benzyl alcohol in an organic phase of 100 cm³, 0.088 gmol of H₂O₂ in 50 cm³ aqueous phase, 0.00001 gmol/cc PTC (TBAB) concentration and 0.00001 gmol/cc co-catalyst (Na₂WO₄.2H₂O) concentration. The conversion of 4-methoxy benzyl alcohol increases with increase in temperature in the range 30°C to 60°C. Thermal decomposition of hydrogen peroxide may become significant at temperatures above 60°C, so the maximum temperature used in the experiments was 60°C.

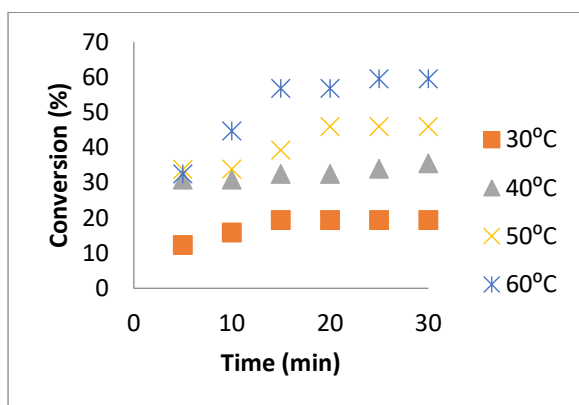


Fig. 4: Effect of Temperature on Oxidation of 4-methoxybenzyl alcohol

4.2.3. Activation Energy

According to Arrhenius law,

$$\ln(r_2/r_1) = E/R (1/T_1 - 1/T_2), \text{ where}$$

E is activation energy, r₁ is rate of reaction at T₁, r₂ is rate of reaction at T₂ and R is universal gas constant.

From the conversion at different temperatures the activation energy was calculated. For T₁= 303K and T₂= 313K activation energy is 17.42 kcal/mol, for T₁= 313K and T₂= 323K activation energy is 19.14 kcal/mol and for T₁= 323K and T₂= 333K activation energy is 19.75 kcal/mol. Thus, the average activation energy was found to be 18.77 kcal/mol.

4.2.4. Effect of Concentration of 4-methoxybenzyl alcohol:

The effect of concentration of 4-methoxy benzyl alcohol was studied by varying its concentration from 0.00022 gmol/cc to 0.00088 gmol/cc under otherwise similar conditions (0.088 gmol of H₂O₂ in 50 cm³ aqueous phase, 0.00001 gmol/cc PTC concentration and 0.00001 gmol/cc co-catalyst concentration, temperature=60°C, 1500 rpm). It is observed that conversion of 4-methoxy benzyl alcohol increases with increasing concentration of 4-methoxy benzyl alcohol shown in Figure 5. The plot of initial rate of reaction versus concentration of 4-methoxy benzyl alcohol is shown in Figure 6. The initial rate of reaction increases with increase in concentration of 4-methoxy benzyl alcohol. The plot of initial rate of reaction versus concentration of 4-methoxy benzyl alcohol is a straight line which suggests that it is a first-order reaction.

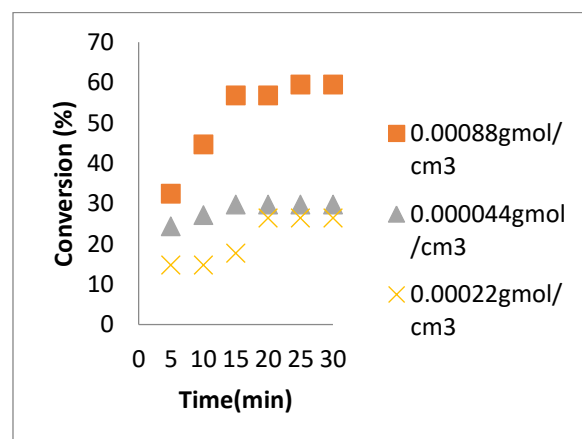


Fig. 5: Effect of Concentration of 4-methoxybenzyl alcohol.

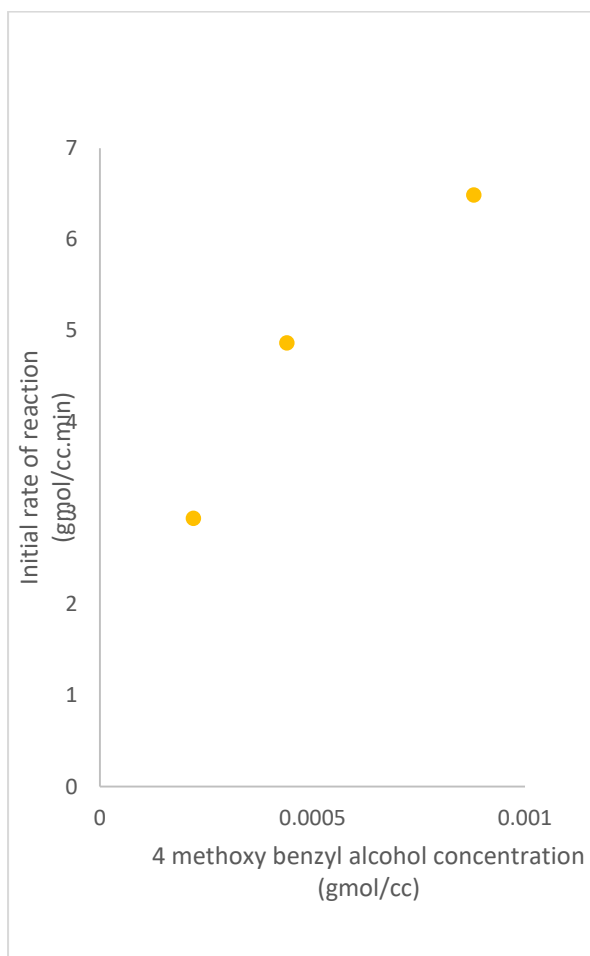


Fig. 6: Initial Rate of Reaction V/s Concentration of 4-methoxybenzyl alcohol.

4.2.5. Effect of Concentration of Hydrogen Peroxide

The effect of concentration of hydrogen peroxide on the conversion of 4-methoxybenzyl alcohol was studied as shown in Figure 7. The concentration of hydrogen peroxide was varied from 0.00044 gmol/cc to 0.00176 gmol/cc in the aqueous phase under otherwise similar conditions (0.088 gmol of 4-methoxybenzyl alcohol in an organic phase of 100 cm³, 0.001 gmol PTC (TBAB) concentration and 0.0005 gmol co-catalyst (Na₂WO₄·2H₂O) concentration, 1500 rpm and temperature=60°C). It is observed that the conversion of 4-methoxybenzyl alcohol in the organic phase increases as the concentration of hydrogen peroxide in the aqueous phase increases. The plot of initial rate of reaction versus concentration of hydrogen peroxide is shown in Figure 8. It is observed that 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.

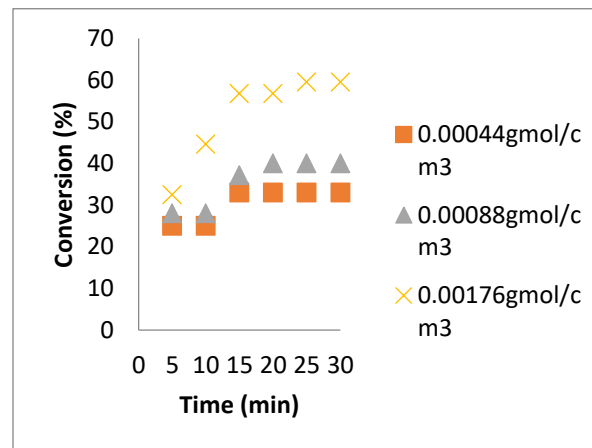


Fig. 7: Effect of Concentration of Hydrogen Peroxide (H₂O₂)

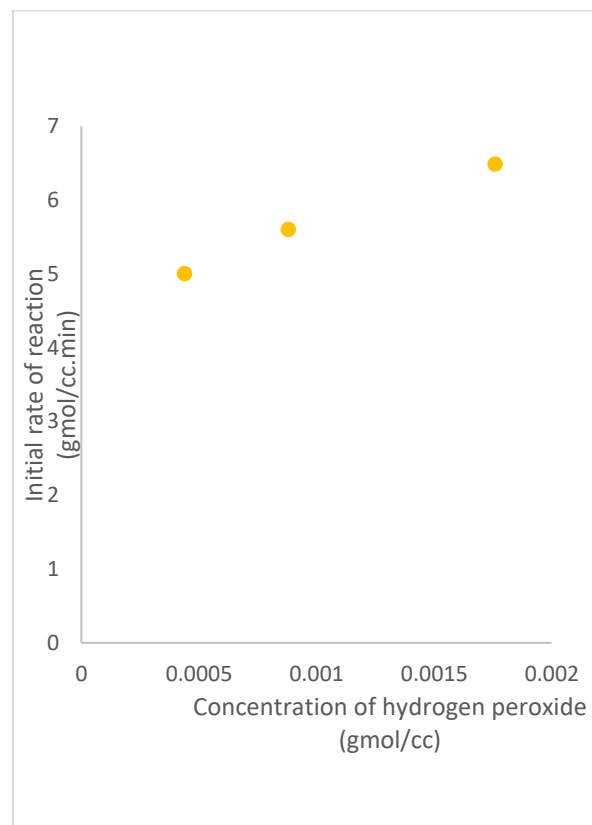


Fig. 8: Initial Rate of Reaction V/s Concentration of H₂O₂

4.2.6. Effect of Phase Transfer Catalyst Concentration

The effect of phase transfer catalyst (tetra butyl ammonium bromide) concentration on the conversion of 4-methoxy benzyl alcohol was studied as shown in Figure 9. The concentration of PTC was varied from 0.0000025 gmol/cc to 0.00001 gmol/cc under otherwise similar conditions (0.088 gmol of 4 methoxy benzyl alcohol in an organic phase of 100cm³, 0.088 gmol H₂O₂ in 50 cm³ aqueous phase, 0.00001 gmol/cc co-catalyst (Na₂WO₄.2H₂O) concentration, 1500 rpm and temperature=60⁰C). It is observed that the conversion of 4-methoxy benzyl alcohol increases with increasing concentration of the phase transfer catalyst. The plot of initial rate of reaction versus the concentration of phase transfer catalyst is shown in Figure 10. As the concentration of PTC increases the initial rate of reaction also increases.

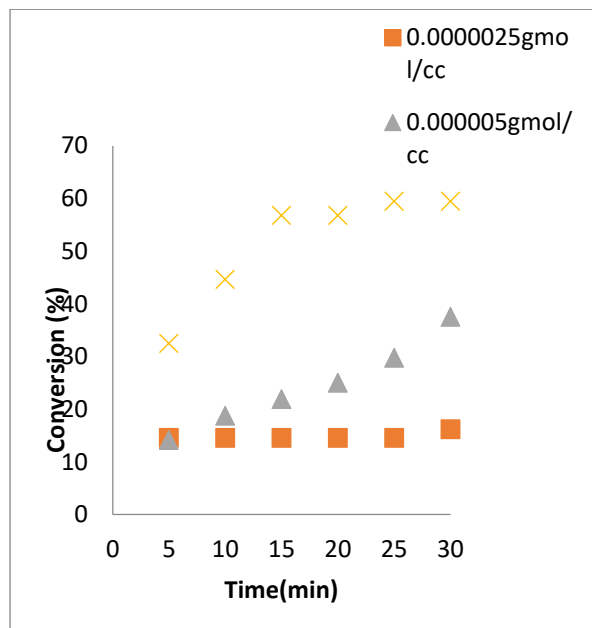


Fig. 9: Effect of Phase Transfer Catalyst Concentration.

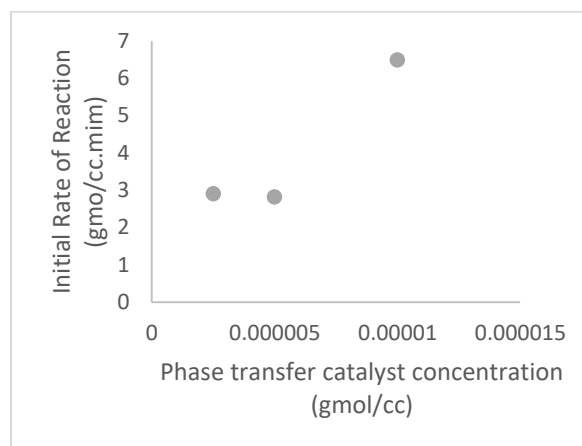


Fig. 10: Initial Rate of Reaction V/s Concentration of PTC

4.2.7. Effect of Co-catalyst Concentration

The effect of co-catalyst (sodium tungstate, Na₂WO₄.2H₂O) concentration on the conversion of 4-methoxy benzyl alcohol was studied as shown in Figure 11 by varying the concentration of sodium tungstate from 0.000005 gmol/cc to 0.00001 gmol/cc under otherwise similar conditions (0.088 gmol of 4-methoxy benzyl alcohol in an organic phase of 100cm³, 0.088 gmol H₂O₂ in 50 cm³ aqueous phase, 0.00001 gmol/cc PTC (TBAB) concentration, 1500 rpm and temperature=60⁰C). It is observed that the conversion of 4-methoxy benzyl alcohol increases with increase in the concentration of the co-catalyst. The plot of initial rate of reaction versus concentration of co-catalyst is shown in Figure 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.

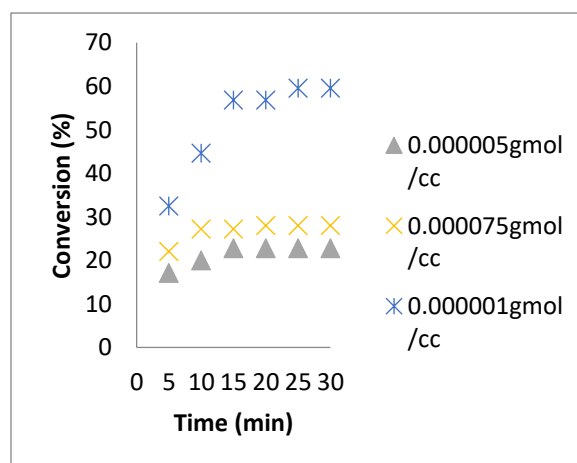


Fig. 11: Effect of Co-catalyst Concentration.

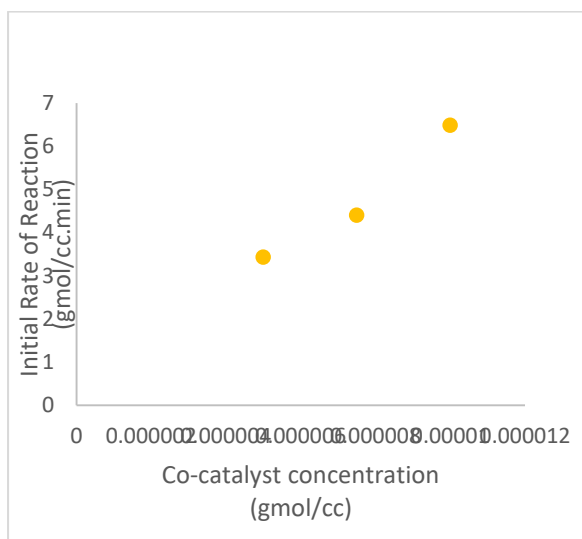


Fig. 12: Initial Rate of Reaction V/s Concentration of Co-catalyst

5. Conclusion

The liquid-liquid phase transfer catalytic oxidation of 4-methoxy benzyl alcohol using hydrogen peroxide as an oxidizing agent has been carried out successfully. Phase transfer catalyst used was TBAB (tetra butyl aluminum bromide) and sodium tungstate was used as a co catalyst. The effect of speed of agitation, temperature, concentration of 4-methoxy benzyl alcohol in the organic phase, concentration of hydrogen peroxide (H_2O_2) in the aqueous phase, concentration of sodium tungstate ($Na_2WO_4 \cdot 2H_2O$) in the aqueous phase and concentration of phase transfer catalyst in the organic phase on the initial rate of reaction was investigated as well as the conversion of 4 methoxy benzyl alcohol versus time profiles for the effect of each of these reaction parameters were plotted. It was observed that the conversion of 4 methoxy benzyl alcohol increases with temperature, concentration 4-methoxy benzyl alcohol in the organic phase, concentration of hydrogen peroxide in aqueous phase, phase transfer catalyst concentration and co-catalyst concentration.

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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