

# Environmentally Friendly Phase Transfer Catalytic Oxidation of Benzhydrol to Benzophenone using Hydrogen Peroxide

Mrs. Trupti G. Holkar<sup>1</sup>, Prof. U. W. Khandalkar<sup>2</sup>, Prof. (Mrs.) P.R. Angre<sup>3</sup>  
and Dr. C. K. Mistry<sup>4</sup>

*Department of Chemical Engineering<sup>1,2,3,4</sup>, Mahatma Gandhi Mission's College of Engineering & Technology, Navi Mumbai<sup>1,2,3,4</sup>*

*Email: truptiholkar88@gmail.com<sup>1</sup>, umakantkhandalkar@gmail.com<sup>2</sup>, prajaktaangre752007@gmail.com<sup>3</sup>, cyruskmistry@gmail.com<sup>4</sup>*

**Abstract-** The concept of phase transfer catalysis involves using a catalyst which facilitates the migration of a reactant in a heterogeneous system from one phase into another phase where reaction can take place. It also enhances the reaction rate of an organic-water system by addition of a catalyst which alters 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 benzophenone from benzhydrol using hydrogen peroxide as the oxidizing agent under phase transfer catalytic conditions with sodium tungstate as a co-catalyst has been reported. Applications where solventless environmentally friendly oxidation reactions using hydrogen peroxide are required are diverse, ranging from pulp and textile bleaching to production of fine chemicals. The kinetics of the oxidation reaction under liquid-liquid phase transfer catalysis was investigated using tetra butyl ammonium bromide (TBAB) as a phase transfer catalyst. The effect of various parameters such as speed of agitation, temperature, concentration of benzhydrol, concentration of H<sub>2</sub>O<sub>2</sub>, phase transfer catalyst loading and co-catalyst loading on the conversion of benzhydrol was studied. A kinetic model for the above-mentioned environmentally friendly catalytic oxidation system was also developed.

**Index Terms-** Heterogeneous Catalysis; Environmentally Friendly Oxidation; Selective Oxidation; Benzophenone; Phase Transfer Catalysis; Kinetic Model.

## 1. INTRODUCTION

A variety of organic reactions have recently been reported to be catalyzed by tetralkylammonium salts. The generation of dichlorocarbene, the alkylation of carbonyl and related compounds, nucleophilic substitution and the benzhydrol condensation are among the reactions which are facilitated by this approach. Two common features of these seem essential: the system has two phases consisting of a water layer and an organic layer and involves an anion as a base or nucleophile. Several explanations have been proposed for the effectiveness of quaternary ammonium ion but the phase transfer mechanism proposed by Starks accounts for the major features of the reaction. Liquid phase catalytic oxidation of alcohols is a fascinating reaction and is one of the most important synthetic reactions in organic chemistry. Oxidation of benzhydrol to benzophenone has been extensively

studied for the production of fine chemicals. Benzhydrol has numerous industrial applications; it is used in perfume and pharmaceutical manufacture and production of agrochemicals. In pharmaceuticals it is used as antiallergenic and antihypertensive agent. On oxidation benzhydrol is converted to benzophenone. Benzophenone is an organic compound used as photo initiator in ultraviolet curing application in the printing industry. It allows manufacturers to package the product in clear glass or plastic (such as PETE water bottle). The oxidative transformation of benzhydrol to benzophenone 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 viz. permanganate, dichromate or chromic acid yielded chiefly benzaldehyde, benzoic acid and only a trace of benzophenone [1,2].

In this research work the selective oxidation of benzhydrol to benzophenone 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. No organic solvent was used in this oxidation and hydrogen peroxide is a clean oxidizing agent which produces water as the only by-product which makes the reaction environmentally friendly.

## 2. MATERIAL

Benzhydrol (LR grade) was obtained from Vasudha Chemicals Pvt. Ltd., Mumbai, India. Hydrogen Peroxide ( $\text{H}_2\text{O}_2$  - 30% w/v solution), Sodium Tungstate ( $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ) and Tetrabutyl Ammonium Bromide (TBAB) of 99.5% purity were obtained from M/s Merck Specialties Pvt. Ltd, Mumbai.

## 3. PROCEDURE

The reactions are carried out batch-wise with necessary safety precautions, in a fully baffled mechanically agitated glass reactor of capacity 500 cm<sup>3</sup>. 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  $\pm 1^\circ\text{C}$ . Typical liquid-liquid PTC reactions were conducted by taking 30 % w/v hydrogen peroxide solution (0.1 gmol of  $\text{H}_2\text{O}_2$ ) adding sodium tungstate (0.001 gmol) and the total volume of the aqueous phase was made up 50 cm<sup>3</sup> by adding distilled water to it. Then the required amount of benzhydrol (0.1 gmol) which forms the organic phase when heated to  $70^\circ\text{C}$  is added to the 50 cm<sup>3</sup> aqueous phase. Then the whole solution was added to the 500 cm<sup>3</sup> glass reactor. The required amount of phase transfer catalyst (PTC) namely TBAB (0.002 gmol) was then added to the reaction mixture and this mixture was stirred at the required speed of agitation at the required temperature ( $70^\circ\text{C}$ ) for the desired time period.

## 4. RESULTS AND DISCUSSION

### 4.1. Mechanism of reaction and kinetic model

The mechanism shown in Fig.1 explains a range of experimental findings in the oxidation of alcohols including benzhydrol. In an aqueous phase, the catalyst precursor  $\text{Na}_2\text{WO}_4$  is rapidly oxidized by  $\text{H}_2\text{O}_2$  according to the reaction:  $\text{Na}_2\text{WO}_4 + 2\text{H}_2\text{O}_2 \rightarrow \text{Na}_2[\text{WO}(\text{O}_2)_2(\text{OH})_2] + \text{H}_2\text{O}$ . 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  $\text{Q}^+$ . In a pH range above 4, the catalytic system that contains largely A has only weak oxidative activity even in the presence of  $\text{Q}^+$ . Since the pKa 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  $\text{HSO}_4^-$  ion is largely deprotonated to  $\text{SO}_4^{2-}$ . Under such dilute conditions, B exists mostly as a monomer. Its anion moiety can easily be transferred to an organic phase by  $\text{Na}^+ - \text{Q}^-$  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 a ketone product (such as benzophenone) and G.

The alkoxy ligand in F is dehydrogenated by the adjacent hydroperoxy ligand via a six-membered transition state where the hydridic  $\alpha$ -hydrogen migrates to the positively polarized oxygen atom. The monoperoxo tungstate ion in G is reoxidized by  $\text{H}_2\text{O}_2$  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.  $\text{H}_2\text{WO}_4$ , a  $\text{Na}^+$ - free compound, acts as an excellent precatalyst but only with a PTC because of the operation of the same mechanism in the biphasic system.

Kinetic models for phase transfer catalysed reactions have been developed by a number of researchers [3-10].

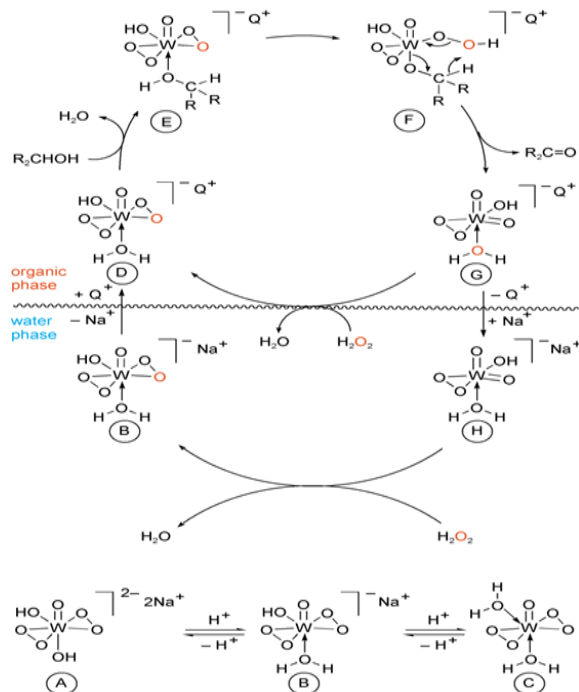
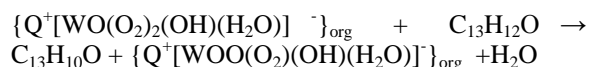
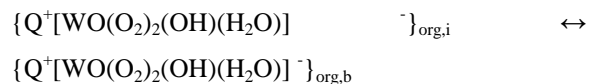


Fig. 1: Catalytic Cycle of Alcohol Oxidation using PTC-H<sub>2</sub>O<sub>2</sub>-Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O system.

Based on the above mechanism, reaction between the quaternary ammonium pair {Q<sup>+</sup>[WO(O<sub>2</sub>)<sub>2</sub>(OH)(H<sub>2</sub>O)]<sup>-</sup>} and benzhydrol in the organic phase is:



While developing a kinetic model for this reaction system it has been assumed that the rate limiting step is the transfer of the quaternary ammonium pair {Q<sup>+</sup>[WO(O<sub>2</sub>)<sub>2</sub>(OH)(H<sub>2</sub>O)]<sup>-</sup>} from the organic phase interface to the bulk organic phase :



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

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

$$r = -\frac{d[C_{14}H_{12}O_2]}{dt} = R_{ca} = k_{LCa}([Q^+[WO(O_2)_2(OH)(H_2O)]^-\}_{org,i} - [Q^+[WO(O_2)_2(OH)(H_2O)]^-\}_{org,b}) \quad \text{(Equation 1)}$$

where r denotes the intrinsic rate of chemical reaction of benzhydrol to benzophenone in the organic phase.

R<sub>ca</sub> = Volumetric rate of transfer of {Q<sup>+</sup>[WO(O<sub>2</sub>)<sub>2</sub>(OH)(H<sub>2</sub>O)]<sup>-</sup>} from the interface to the bulk organic phase,

k<sub>LCa</sub> = Mass transfer coefficient for transfer of {Q<sup>+</sup>[WO(O<sub>2</sub>)<sub>2</sub>(OH)(H<sub>2</sub>O)]<sup>-</sup>} from the interface to the bulk organic phase,

a = Interfacial area per unit volume of the organic phase.

If the reaction system conforms to the Slow Reaction Regime (Regime 2), then there will be no free {Q<sup>+</sup>[WO(O<sub>2</sub>)<sub>2</sub>(OH)(H<sub>2</sub>O)]<sup>-</sup>} present in the bulk organic phase i.e. [Q<sup>+</sup>[WO(O<sub>2</sub>)<sub>2</sub>(OH)(H<sub>2</sub>O)]<sup>-</sup>]<sub>org,b</sub> = 0 and the following rate equation will be valid:

$$R_{ca} = k_{LCa} [Q^+[WO(O_2)_2(OH)(H_2O)]^-\}_{org,i} \quad \text{(Equation 2)}$$

#### 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

To ascertain the influence of mass transfer limitations in the L-L PTC oxidation of benzhydrol with H<sub>2</sub>O<sub>2</sub>, the speed of agitation was varied in the range of 300-1500 rpm otherwise similar conditions (namely, 0.1 gmol benzhydrol as organic phase, 50 cm aqueous phase containing 0.1 gmol H<sub>2</sub>O<sub>2</sub>, 0.001

gmol of sodium tungstate, 0.002gmol of PTC (TBAB) loading, temperature = 343K) as shown in Fig. 2. The conversion of benzhydrol was found to increase when the speed of agitation was increased from 300 to 1500 rpm. This suggests that mass transfer effects may be 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 dependent of the speed of agitation as shown in Fig. 3. This shows that there is some mass transfer limitation in this oxidation reaction. Thus, the experimental results obtained indicate that mass transfer effects are significant in the oxidation reaction.

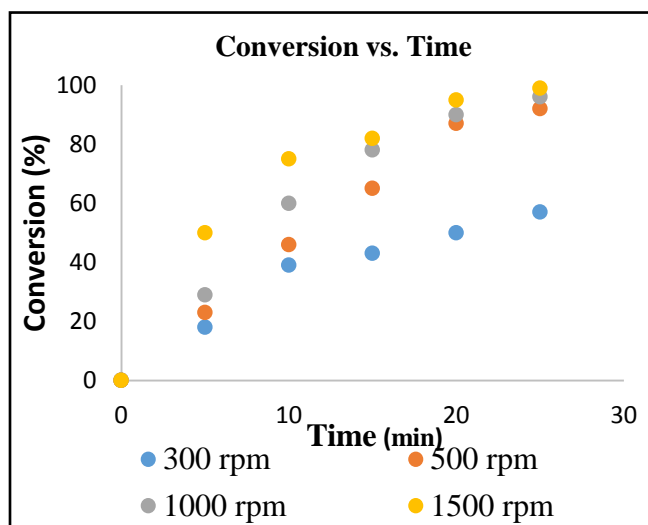


Fig. 2: Effect of Speed of Agitation on Oxidation of Benzhydrol

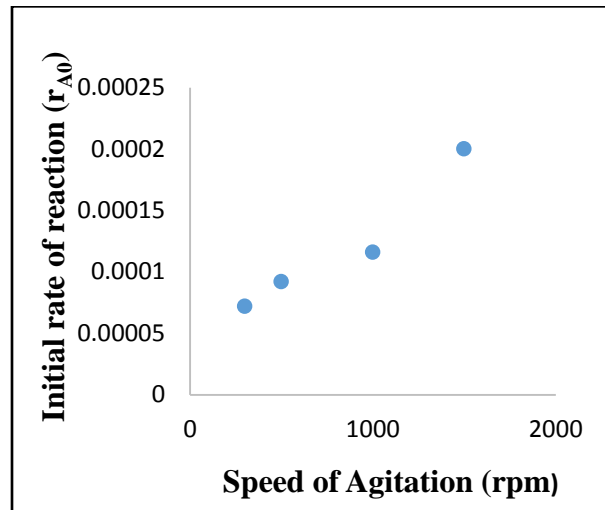


Fig. 3 : Initial Rate of Reaction V/s Speed of Agitation

#### 4.2.2. Effect of temperature

The effect of temperature on the oxidation of benzhydrol was studied by varying the temperature from 50°C (323K) to 70°C (343K) under otherwise similar conditions (namely, 0.1 gmol benzhydrol as organic phase, 50 cm<sup>3</sup> aqueous phase containing 0.1 gmol H<sub>2</sub>O<sub>2</sub>, 0.001 gmol of sodium tungstate, 0.002gmol of PTC (TBAB) loading, speed of agitation = 300 rpm) as shown in Fig. 4. The conversion of benzhydrol was observed to increase with increase in reaction temperature. Thermal decomposition of hydrogen peroxide may be significant at temperatures of 70°C and above. The calculated activation energy from plot for the temperature range of 50°C-70°C is 6.48 kcal/gmol (Fig. 5), which indicates that mass transfer effects are significant and reaction is not kinetically controlled.

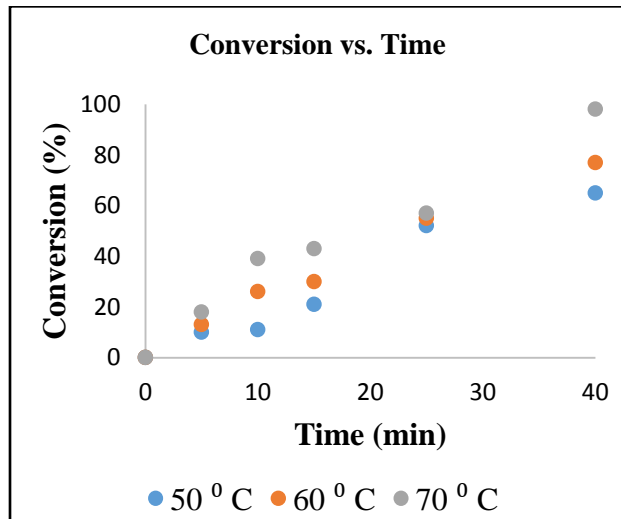


Fig. 4: Effect of Temperature on Oxidation of Benzhydrol

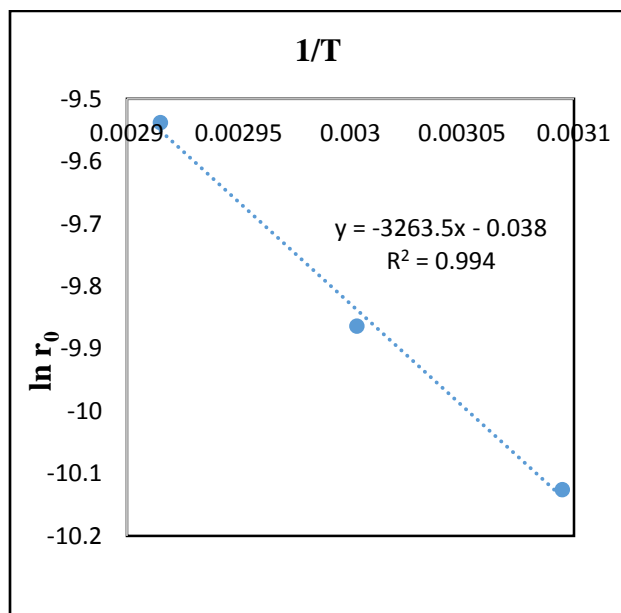


Fig. 5 : Arrhenius Plot

#### 4.2.3. Effect of concentration of benzhydrol:

The effect of concentration of benzhydrol was studied by varying the concentration of benzhydrol in the organic phase from 0.09 gmol/cc to 0.14 gmol/cc under otherwise similar conditions

(namely, 50 cm<sup>3</sup> aqueous phase containing 0.1 gmolH<sub>2</sub>O<sub>2</sub>, 0.001 gmol of sodium tungstate, 0.002gmol of PTC (TBAB) loading, temperature = 343K, speed of agitation = 300 rpm) as shown in Fig. 6. The conversion of benzhydrol was observed to increase with increase in the concentration of benzhydrol in the organic phase. A plot of initial rate of reaction versus concentration of benzhydrol shows that the initial rate of reaction remains practically constant as the concentration of benzhydrol increases as shown in Fig. 7. This suggests that the reaction may be zero order with respect to the concentration of benzhydrol in the concentration range studied. A plot of concentration of benzhydrol versus time was also found to be a straight line as shown in Fig. 8 which suggests zero order behaviour and the zero order rate constant evaluated from the slope of the plot was found to be 0.002 gmol/cc.min.

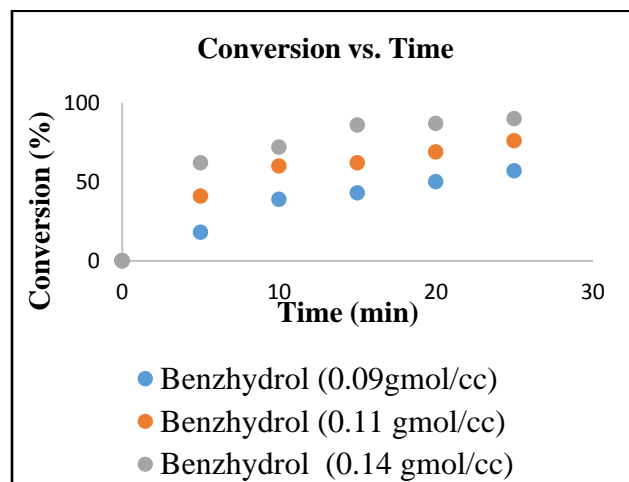


Fig. 6: Effect of Concentration of Benzhydrol

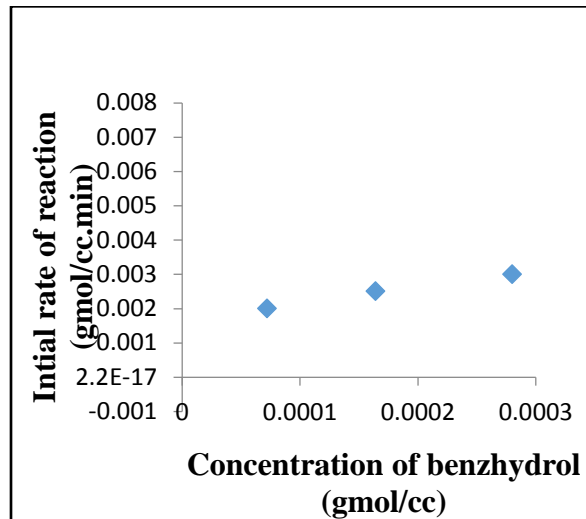


Fig. 7: Initial Rate of Reaction V/s Concentration of Benzhydrol.

#### 4.2.4. Effect of concentration of hydrogen peroxide

The effect of concentration of the oxidizing agent, namely hydrogen peroxide ( $H_2O_2$ ), in the aqueous phase on oxidation reaction was studied by varying the concentration of hydrogen peroxide in the aqueous phase from  $0.0015 \text{ gmol/cm}^3$  to  $0.002 \text{ gmol/cm}^3$  under otherwise similar conditions (namely,  $0.1 \text{ gmol}$  benzhydrol as organic phase,  $50 \text{ cm}^3$  aqueous phase containing  $H_2O_2$ ,  $0.001 \text{ gmol}$  of sodium tungstate,  $0.002 \text{ gmol}$  of PTC (TBAB) loading, temperature =  $343\text{K}$ , speed of agitation =  $300 \text{ rpm}$ ) as shown in Fig. 9. The conversion of benzhydrol was observed to increase with decrease in the concentration of hydrogen peroxide in the aqueous phase. This may occur since as the concentration of hydrogen peroxide decreases the mole ratio of benzhydrol to hydrogen peroxide increases. A plot of rate of reaction versus concentration of hydrogen peroxide in the aqueous phase was prepared as shown in Fig. 10 and it was observed that the rate of reaction was found to be linearly dependent of the concentration of hydrogen peroxide in the concentration range studied. This suggests that the reaction may be first order with respect to the concentration of hydrogen peroxide in the concentration range studied.

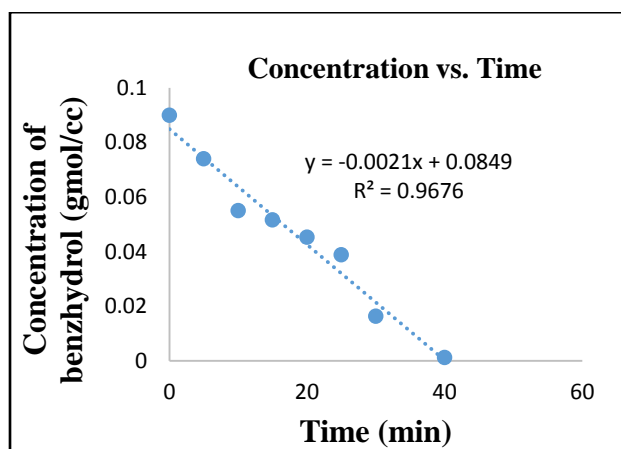


Fig. 8: Zero order Kinetics Plot of Benzhydrol.

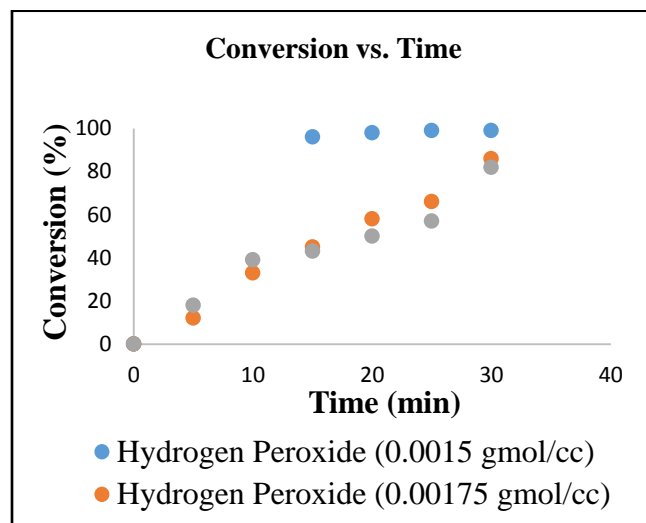


Fig. 9: Effect of Concentration of Hydrogen Peroxide ( $H_2O_2$ )

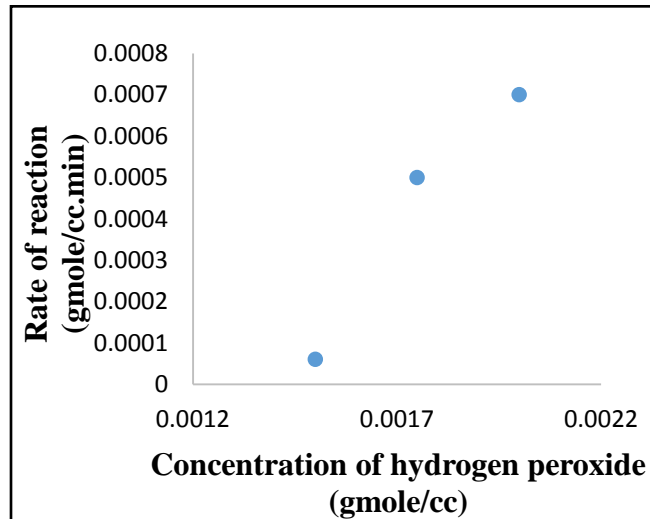


Fig. 10: Rate of Reaction V/s Concentration of H<sub>2</sub>O<sub>2</sub>

#### 4.2.5. Effect of phase transfer catalyst loading

The effect of phase transfer catalyst loading on the oxidation of benzhydrol was studied by varying the phase transfer catalyst (tetra butyl ammonium bromide, TBAB) loading from 0.002 gmol to 0.006 gmol (based on benzhydrol) under otherwise similar conditions (namely, 0.1 gmolbenzhydrol as organic phase, 50 cm<sup>3</sup> aqueous phase containing 0.1 gmol H<sub>2</sub>O<sub>2</sub>, 0.001 gmol of sodium tungstate, temperature = 343K, speed of agitation = 300 rpm) as shown in Fig. 11. The conversion of benzhydrol was observed in general to increase with increase in the phase transfer catalyst loading for the range of catalyst loadings studied. A plot of initial rate of reaction versus total concentration of the phase transfer catalyst in the organic phase was prepared as shown in Fig. 12 and it was observed that the initial rate of reaction was linearly dependent on the total concentration of phase transfer catalyst in the organic phase for the concentration range studied. This suggests that the reaction may be first order with respect to the total concentration of phase transfer catalyst in the organic phase for the concentration range studied.

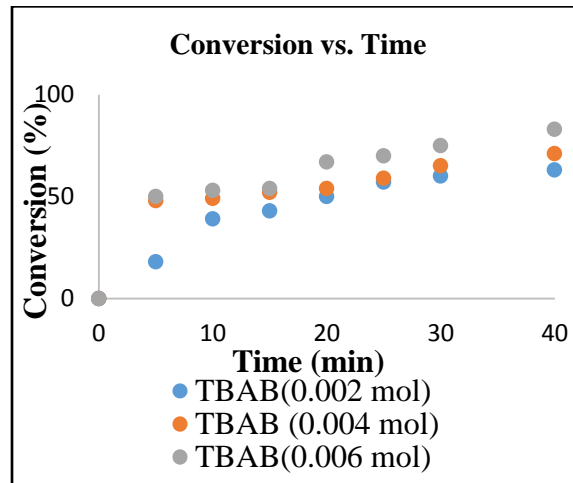


Fig. 11: Effect of Phase Transfer Catalyst Loading

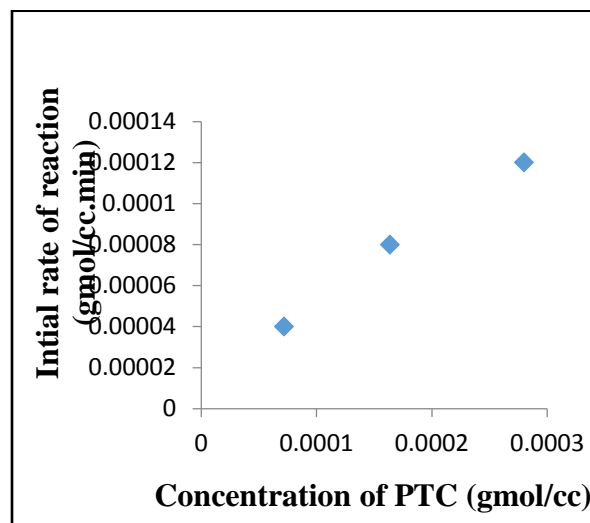


Fig. 12: Initial Rate of Reaction V/s Total Concentration of PTC

#### 4.2.6. Effect of co-catalyst loading

The effect of co- catalyst loading on the oxidation of benzhydrol was studied by varying the co-catalyst (sodium tungstate, Na<sub>2</sub>WO<sub>4</sub>.2H<sub>2</sub>O)loading from 0.001 gmol to 0.002 gmol (based on benzhydrol) under otherwise similar conditions (namely, 0.1 gmol benzhydrol, as organic phase 50 cm<sup>3</sup> aqueous phase containing 0.1 gmol H<sub>2</sub>O<sub>2</sub>, 0.002gmol of PTC (TBAB) loading, temperature = 343K, speed of agitation = 300 rpm) as shown in Fig. 13. The conversion of benzhydrol was observed in general to increase with increase in the co-catalyst loading for the range of co-catalyst loadings studied. A plot of initial rate of reaction versus concentration of the co-catalyst in the aqueous phase was prepared as shown

in Fig. 14 and it was observed that the initial rate of reaction was linearly dependent on the concentration of co-catalyst in the aqueous phase for the concentration range studied. This suggests that the reaction may be first order with respect to the concentration of the co-catalyst in the aqueous phase.

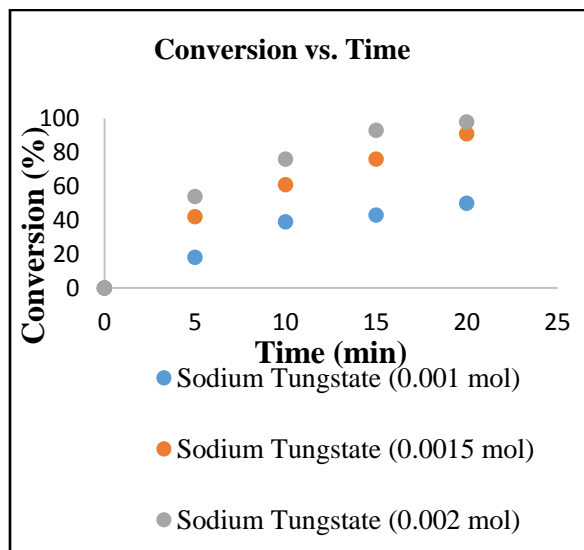


Fig. 13: Effect of Co-catalyst Loading

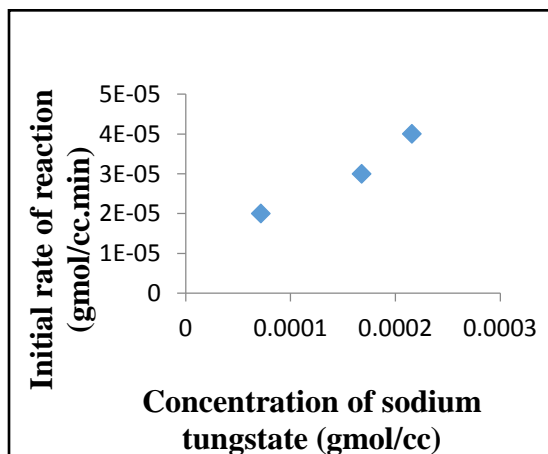


Fig. 14: Initial Rate of Reaction V/s Concentration of Co-catalyst

## 5. CONCLUSION

The oxidation of benzhydrol to benzophenone was successfully carried out with hydrogen peroxide as an oxidizing agent under liquid-liquid phase transfer catalysis with tetrabutyl

ammonium bromide as the phase transfer catalyst and sodium tungstate as the co-catalyst. It was observed that the conversion of benzhydrol increases with temperature, concentration of benzhydrol in the organic phase, phase transfer catalyst loading and co-catalyst loading. The reaction may be considered to be mass transfer controlled at a speed of agitation. Arrhenius plot indicates that mass transfer limitations are important and suggests that the reaction is not kinetically controlled. A suitable reaction mechanism and a theoretical model have been proposed to explain the experimental results obtained as a part of this research work.

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