

# Oxidation of Benzoin to Benzil under Liquid-Liquid Phase Transfer Catalysis with Hydrogen Peroxide as the Oxidizing Agent

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**Abstract-** Phase transfer catalysis is an attractive technique for organic synthesis involving two or more insoluble phases because of its advantages of mild operating conditions, high selectivity and enhanced rates of reaction. The catalytic oxidation with hydrogen peroxide in aqueous solutions offers an economic and environmentally safe alternative to other oxidation reactions performed in synthetic laboratories and chemical industry. Hydrogen peroxide contains 47% active oxygen and the only by-product formed is water. In searching for a more efficient oxidation process, we have focused our attention toward the development of green reagent. Here, we report that the selective oxidation of Benzoin to Benzil 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. The kinetics of this oxidation reaction is being investigated by studying the effect of various parameters such as speed of agitation, temperature, concentration of benzoin, concentration of H<sub>2</sub>O<sub>2</sub>, phase transfer catalyst loading, and co-catalyst loading. It is also proposed to develop a theoretical model for the above-mentioned environmentally friendly catalytic oxidation system.

**Index Terms-** Environmentally Friendly Oxidation, Selective Oxidation, Benzil, Phase Transfer Catalysis, Kinetic Model.

## 1. INTRODUCTION

A variety of organic reactions have recently been reported to be catalyzed by tetraalkylammonium salts. The generation of dichlorocarbene, the alkylation of carbonyl and related compounds, nucleophilic substitution and the benzoin 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 benzoin to benzil has been extensively studied for the production of fine chemicals. In general  $\alpha$ -dicarbonyl compounds are important synthetic intermediates in the synthesis of many heterocyclic compounds.  $\alpha$ -Dicarbonyl compounds have diverse applications in organic and pharmaceutical industries such as photosensitive and synthetic reagents and photo initiators for radical polymerization. Benzil, in particular, is a standard building block in organic synthesis and is utilized as an intermediate in the synthesis of chiral ligands and biologically active compounds. The oxidative transformation of an  $\alpha$ -hydroxy ketone to the corresponding  $\alpha$ -diketone (benzoin to benzil) 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, bismuth oxide and bismuth nitrate, iron (II) thiolate and oxone, trichlorooxyvanadium and vanadium oxide, titanium (IV) chloride and triethylamine or by molecular oxygen using microwave irradiation on zeolite A or clayfen, or by nickel hydroxalcite activation. The conventional oxidizing agents viz. permanganate, dichromate or chromic acid yielded chiefly benzaldehyde/benzoic acid and only a trace of benzil. The limits of practical utilization of these reagents involves the use of stoichiometric amounts of corrosive acids or toxic metallic reagents, which in turn produce undesirable waste materials and required high reaction temperatures.

In this research work the selective oxidation of Benzoin to Benzil 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.

## 2. MATERIAL

Benzoin of LR grade was obtained from M/s S. D. Fine Chemicals Pvt. Ltd, Mumbai, India. Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub> - 30% w/v Solution), Sodium Tungstate (Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O), Ethyl Acetate and Tetrabutyl Ammonium Bromide (TBAB) of 99.5%

purity were obtained from M/s Merck Specialities Pvt. Ltd, Mumbai, India.

### 3. PROCEDURE

The reaction was carried out in a fully baffled mechanically agitated glass reactor of capacity 500 cm<sup>3</sup> (6.5 cm i.d.) equipped with a three-bladed glass pitched turbine impeller. The reactor was kept in a constant temperature water bath whose temperature could be controlled within ±1°C. The aqueous phase consisting of sodium tungstate (co-catalyst) dissolved in 50 ml of 30 % w/v H<sub>2</sub>O<sub>2</sub> solution was added to the 500 cm<sup>3</sup> glass reactor and then 50 ml of the organic phase consisting of benzoin dissolved in ethyl acetate as solvent was transferred to the aqueous phase in the reactor. The required amount of phase transfer catalyst namely TBAB (0.005 gmol) was then added to the reaction mixture and this mixture was stirred at a specific speed of agitation with the temperature maintained at 60°C for the desired time period (30 min.). The samples of the aqueous phase are collected in the sample bottles at regular intervals and analyzed by using iodometric titration.

### 4. RESULTS & 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 α-hydroxyketones. In an aqueous phase, the catalyst precursor Na<sub>2</sub>WO<sub>4</sub> is rapidly oxidized by H<sub>2</sub>O<sub>2</sub> according to the reaction: Na<sub>2</sub>WO<sub>4</sub> + 2H<sub>2</sub>O<sub>2</sub> → Na<sub>2</sub>[WO(O<sub>2</sub>)<sub>2</sub>(OH)<sub>2</sub>] + H<sub>2</sub>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. The mono-protonated species **B** is dominant under reaction conditions with a pH range of 0.4–3. Its anion moiety can easily be transferred to an organic phase by Na<sup>+</sup>-Q<sup>+</sup> ion exchange. In the organic layer, the bisperoxo complex **D** undergoes water–ketone ligand exchange to form **E**. Then proton transfer in **E** generates the reactive species **F**, which forms a diketone product and **G**. The monoperoxo tungstate ion in **G** is reoxidized by H<sub>2</sub>O<sub>2</sub> 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.

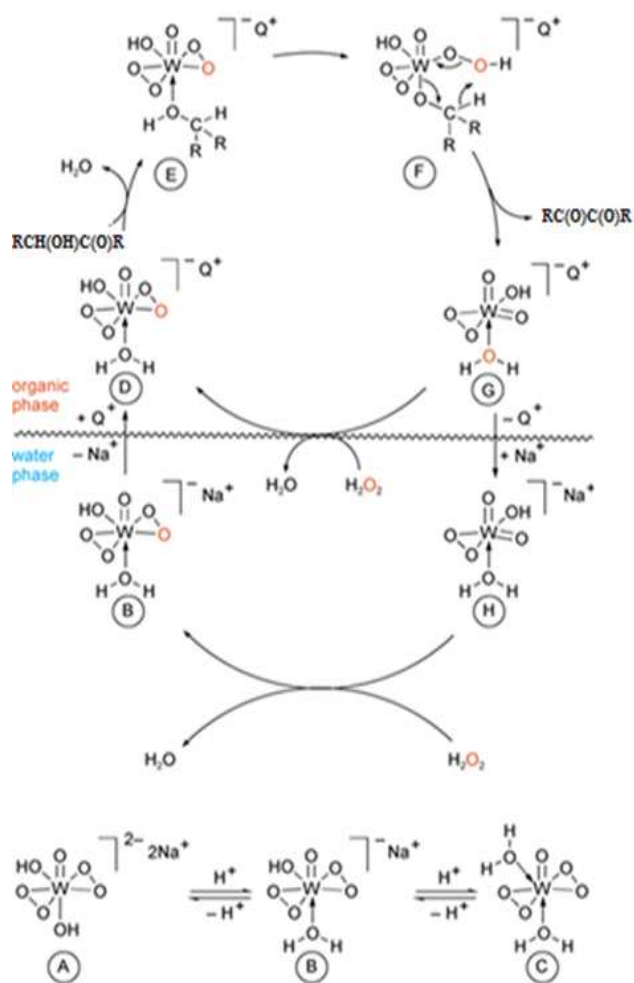
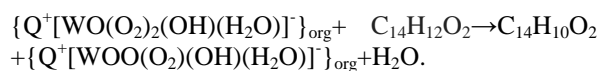


Fig. 1. Catalytic Cycle of α-hydroxyketones Oxidation using PTC-H<sub>2</sub>O<sub>2</sub>-Na<sub>2</sub>WO<sub>4</sub>.2H<sub>2</sub>O system.

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 Benzoin in the organic phase may be represented as follows:



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

$$r = -d[C_{14}H_{12}O_2] / dt = k[Q^+[WO(O_2)_2(OH)(H_2O)]^-\]_{org}[C_{14}H_{12}O_2]_{org}$$

Where r denotes the intrinsic rate of chemical reaction of Benzoin to Benzil in the organic phase.

#### 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 speed of agitation was varied in the range of 500–1800 rpm under otherwise similar conditions (namely, 0.011 gmol Benzoin, organic phase made up to 50 ml with ethyl acetate as solvent, aqueous phase (30% w/v H<sub>2</sub>O<sub>2</sub>) volume = 50 ml, 0.0025 gmol of sodium tungstate, 0.005 gmol of PTC (TBAB) loading, temperature = 333K). It was found that the rate of reaction was found to independent of the speed of agitation as shown in Fig. 2. This shows that mass transfer effects are negligible in this oxidation reaction and that the oxidation reaction is kinetically controlled.

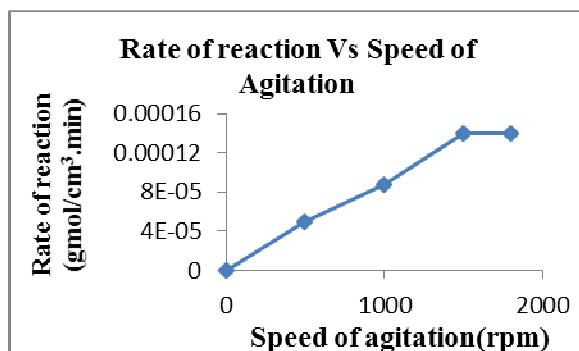


Fig. 2 : Rate of Reaction V/s Speed of Agitation

##### 4.2.2. Effect of temperature

The effect of temperature on the oxidation of Benzoin was studied by varying the temperature from 30°C (303K) to 60°C (333K) under otherwise similar conditions (namely, 0.011 gmol Benzoin, organic phase made up to 50 ml with ethyl acetate as solvent, aqueous phase (30% w/v H<sub>2</sub>O<sub>2</sub>) volume = 50 ml, 0.0025 gmol of sodium tungstate, 0.005 gmol of PTC (TBAB) loading, at specific speed of agitation) as shown in Fig.3. The conversion of Benzoin was observed to increase with increase in reaction temperature up to 60°C. The calculated activation energy from the Arrhenius plot for the temperature range of 30°C-60°C is 10.99/gmol (Fig. 4), which indicates that the reaction is kinetically controlled.

Yellow coloured crystals of benzil were observed to have formed when the reaction was carried out for 30 minutes at 333K and the ethyl acetate solvent was separated by evaporation.

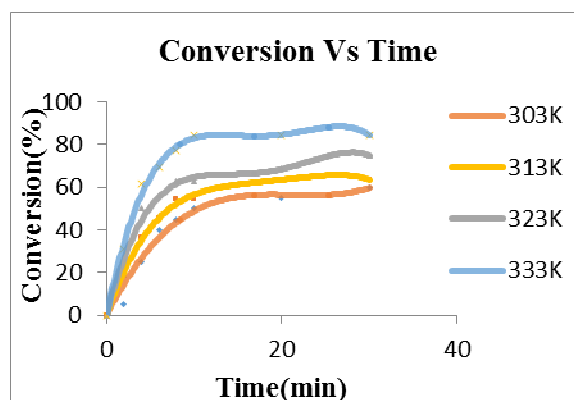


Fig. 3: Effect of Temperature on Oxidation of Benzoin

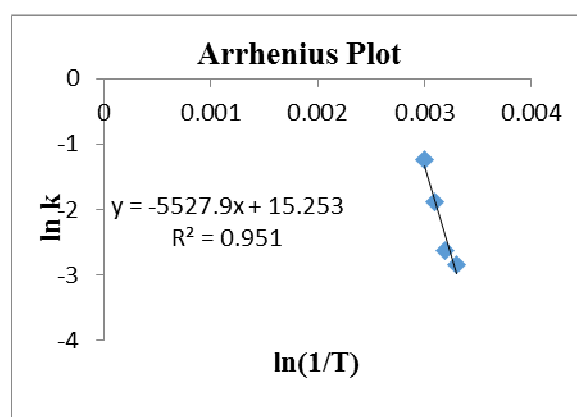


Fig. 4: Arrhenius Plot

##### 4.2.3. Effect of concentration of benzoin

The effect of concentration of Benzoin in the organic phase on the oxidation reaction was studied by varying the concentration of Benzoin in the organic phase from 0.011 gmol/cm<sup>3</sup> to 0.022 gmol/cm<sup>3</sup> under otherwise similar conditions (namely, organic phase made up to 50 ml with ethyl acetate as solvent, aqueous phase (30% w/v H<sub>2</sub>O<sub>2</sub>) volume = 50 ml, 0.0025 gmol of sodium tungstate, 0.005 gmol of PTC (TBAB) loading, at specific speed of agitation, temperature = 333K) as shown in Fig. 5. The conversion of Benzoin was observed to increase with decrease in the concentration of Benzoin in the organic phase. This due to the fact that by decreasing the concentration of Benzoin the mole ratio of H<sub>2</sub>O<sub>2</sub> to Benzoin increases which results in higher rates of oxidation. A plot of  $-\ln(1-X_A)$  versus time (Fig. 6) at 333 K was found to be linear which shows that the reaction is first order with respect to the concentration of Benzoin and this suggests that mass transfer effects are negligible which is in agreement with the high value of activation energy obtained.

When 0.022 gmol of Benzoin was dissolved in 50 ml of ethyl acetate and the organic phase heated to 333K, it

was observed that Benzoin was not completely soluble in ethyl acetate which was used as solvent of hydrogen peroxide during the initial stages of the reaction.

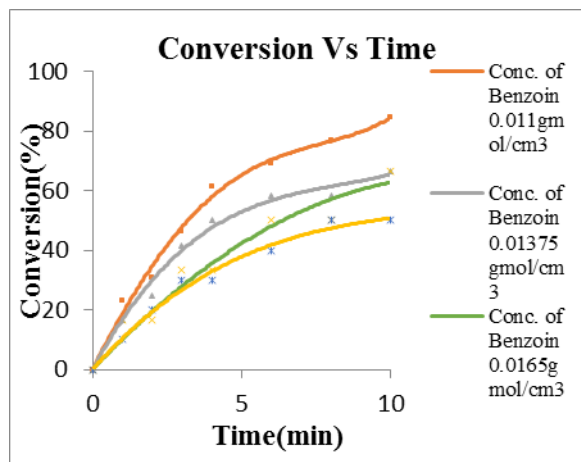


Fig. 5: Effect of Concentration of Benzoin

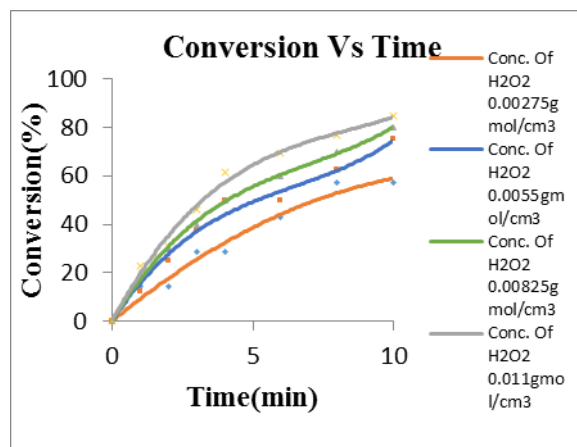


Fig.7: Effect of Concentration of Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>)

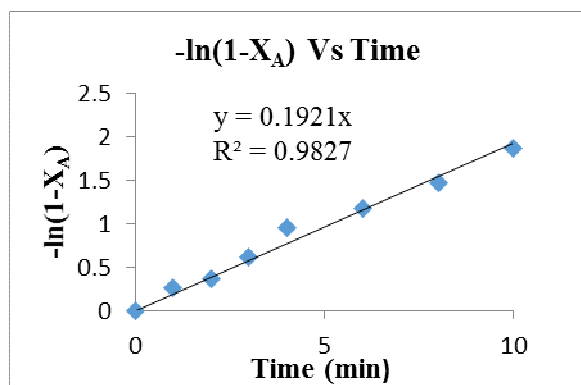


Fig. 6: Plot of  $-\ln(1-X_A)$  V/s Time at 333 K

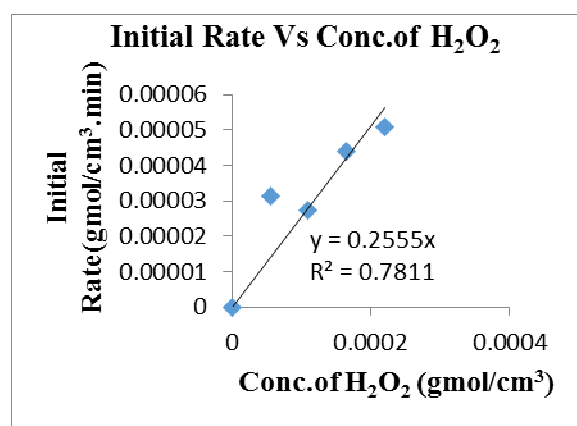


Fig. 8: Initial Rate of Reaction V/s Concentration of H<sub>2</sub>O<sub>2</sub>

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

The effect of concentration of the oxidizing agent, namely hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), in the aqueous phase on oxidation reaction was studied by varying the concentration of hydrogen peroxide in the aqueous phase from 0.00275 gmol/cm<sup>3</sup> to 0.011 gmol/cm<sup>3</sup> under otherwise similar conditions (namely 0.011 gmol benzoin, organic phase made up to 50 ml with ethyl acetate as solvent, aqueous phase (30% w/v H<sub>2</sub>O<sub>2</sub>) volume = 50 ml, 5 mol % of PTC (TBAB) loading, at specific speed of agitation, temperature = 333K) as shown in Fig. 7. The conversion of benzoin was observed to increase with increase in the concentration of hydrogen peroxide in the aqueous phase. A plot of initial rate of reaction versus concentration of hydrogen peroxide in the aqueous phase was prepared as shown in Fig. 8 and it was observed that the initial rate of reaction was linearly dependent on the concentration of hydrogen peroxide in the concentration range studied. This shows that the reaction is first order with respect to the concentration

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

The effect of phase transfer catalyst loading on the oxidation of benzoin was studied by varying the phase transfer catalyst (tetrabutyl ammonium bromide, TBAB) loading from 0.005 gmol to 0.015 gmol (based on benzoin) under otherwise similar conditions (namely, 0.011 gmol benzoin, organic phase made up to 50 ml with ethyl acetate as solvent, aqueous phase (30% w/v H<sub>2</sub>O<sub>2</sub>) volume = 50 ml, 0.0025 gmol of sodium tungstate, at specific speed of agitation, temperature = 333K) as shown in Fig. 9. The conversion of benzoin was observed in general to increase with increase in the phase transfer catalyst loading for the range of catalyst loadings studied.

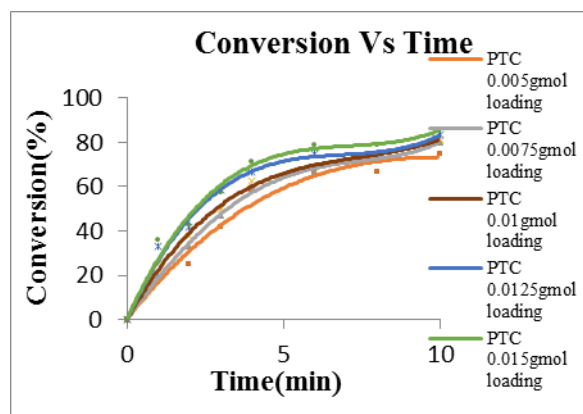


Fig. 9: Effect of Phase Transfer Catalyst Loading

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. 10 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 shows that the reaction is first order with respect to the total concentration of phase transfer catalyst in the organic phase during the initial stages of the reaction.

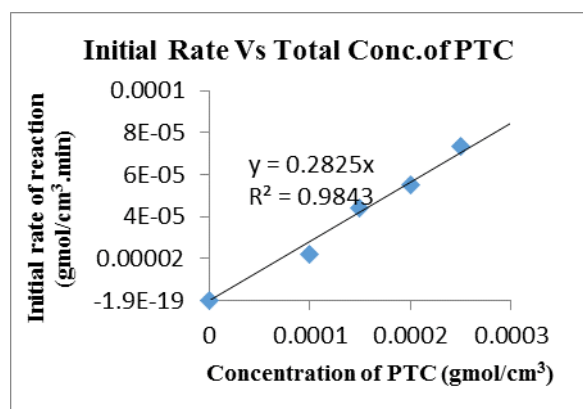


Fig. 10: Initial Rate of Reaction V/s Total Concentration of PTC

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

The effect of co-catalyst loading on the oxidation of benzoin was studied by varying the co-catalyst (sodium tungstate,  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ) loading from 0.001 gmol to 0.0025 gmol (based on benzoin) under otherwise similar conditions (namely, 0.011 gmol benzoin, organic phase made up to 50 ml with ethyl acetate as solvent, aqueous phase (30% w/v  $\text{H}_2\text{O}_2$ ) volume = 50 ml, 0.005 gmol of phase transfer catalyst, at specific speed of agitation, temperature = 333K) as shown in Fig. 11. The conversion of benzoin was observed in general to increase with increase in the co-catalyst loading for the range of co-catalyst loadings studied.

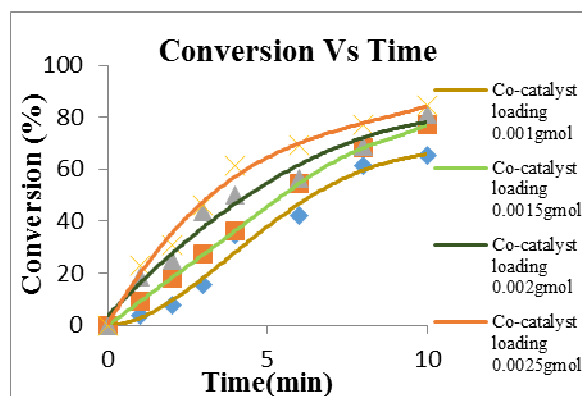


Fig. 11: Effect of Co-catalyst Loading

A plot of initial rate of reaction versus concentration of the co-catalyst in the aqueous phase was prepared as shown in Fig. 12 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 shows that the reaction is first order with respect to the concentration of co-catalyst in the aqueous phase during the initial stages of the reaction.

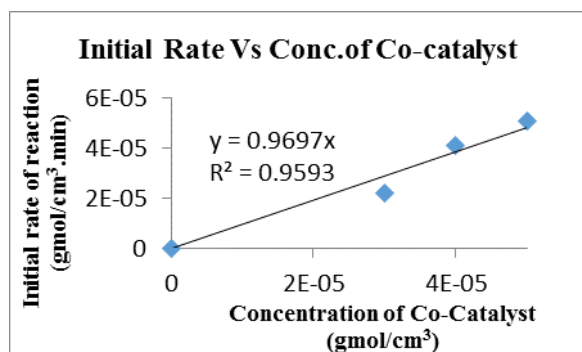


Fig.12: Initial Rate of Reaction V/s Concentration of Co-catalyst

## 5. CONCLUSION

The oxidation of benzoin to benzil 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. It was observed that the conversion of benzoin increases with speed of agitation, temperature and phase transfer catalyst loading. A suitable reaction mechanism and a theoretical model has been proposed to explain the experimental results obtained.

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