

# Environmentally Friendly Oxidation of Cyclohexanol to Cyclohexanone with Hydrogen Peroxide under Liquid-Liquid Phase Transfer Catalysis

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**Abstract:** The goal of this research work is to develop an environmentally friendly catalytic oxidation system for the synthesis of cyclohexanone from cyclohexanol using hydrogen peroxide as the oxidizing agent under phase transfer catalytic conditions with heteropolyacid (dodeca-tungstophosphoric acid) as a co-catalyst. The effect of various reaction parameters is studied for this oxidation system. It was observed that the reaction takes place to a significant extent (89% conversion) in 30 minutes at a temperature of 60°C and a speed of agitation of 1200 rpm. The calculated activation energy from the Arrhenius plot for the temperature range of 40°C-60°C using initial rate of reaction is 1.48 kcal/gmol, which indicates that the reaction may be mass transfer controlled. The initial rate of reaction was independent of the concentration of cyclohexanol in the organic phase for the concentration range studied. The initial rate of reaction was found to be linearly dependent on the concentration of hydrogen peroxide in the aqueous phase, the total concentration of the phase transfer catalyst in the organic phase and the co-catalyst loading. A reaction mechanism is proposed and a kinetic model is developed for this environmentally friendly catalytic oxidation system.

**Keywords:** Cyclohexanone, Environmentally Friendly Oxidation, Heteropolyacid, Hydrogen Peroxide, Kinetic Model, Phase Transfer Catalysis.

## 1. INTRODUCTION

### 2.

Oxidation of organic compounds is an important reaction in laboratory scale organic synthesis as well as in large scale chemical processes [1]. Most of these processes are carried out by using oxidants such as nitric acid, chlorine-containing compounds and high valent transition metal oxides and salts. The use of environmentally friendly oxidizing agents such as hydrogen peroxide and air (or oxygen) is gaining importance in the chemical industry. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is a clean and effective oxidizing agent since it contains 47% of active oxygen and the only by-product formed is water. Since aqueous solutions of H<sub>2</sub>O<sub>2</sub> are immiscible with organic compounds the use of phase transfer catalysts (PTCs) such as Tetra Butyl Ammonium Bromide is recommended in such heterogeneous reactions [2,3]. The use of co-catalysts such as sodium tungstate [4-8] or heteropolyacids [9] with PTCs has proven to be advantageous in intensifying the rates of oxidation reactions with H<sub>2</sub>O<sub>2</sub>.

The oxidation of alcohols particularly the oxidation of cyclohexanol to cyclohexanone plays an important role in organic synthesis [10-13]. Cyclohexanone is mainly used as an intermediate in the production of adipic acid (for nylon 66) and caprolactum (for nylon 6). Cyclohexanone is also used as a solvent for synthetic resins, polymers and lacquers and as a starting material in the synthesis of many insecticides, herbicides and pharmaceuticals [14].

In the present work, an environmentally friendly catalytic oxidation system is developed for the synthesis of cyclohexanone from cyclohexanol 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 heteropolyacid (dodeca-tungstophosphoric acid) as the co-catalyst. The use of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as the oxidizing agent in the presence of PTC gives water as the only by-product which makes the reaction environmentally friendly.

**2. EXPERIMENTAL SECTION****2.1. Materials**

Cyclohexanol 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), dodeca-tungstophosphoric acid [phosphotungstic acid] (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>), ethyl acetate, and tetra butyl ammonium bromide (TBAB) of 99.5% purity were obtained from M/s Merck Specialties Pvt. Ltd, Mumbai, India.

**2.2. Experimental Procedure**

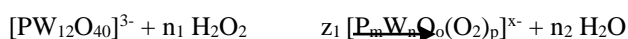
The experimental set-up consists of a batch reactor, which is a fully baffled mechanically agitated glass reactor of capacity 500 cm<sup>3</sup>. A three-bladed glass disk turbine impeller with the provision of speed regulation is used for stirring the reaction mixture. A reflux condenser is connected to the reactor in some experiments especially for reactions carried out at high temperatures. The reactor is kept in a constant temperature water bath whose temperature is controlled within ±1 °C.

Typical liquid-liquid PTC reactions are conducted by taking 0.088 gmol cyclohexanol and adding ethyl acetate as solvent until the total volume of the organic phase is 100 cm<sup>3</sup>. The required amount of phosphotungstic acid (0.0005 gmol) is added to 50 cm<sup>3</sup> of 30 % w/v H<sub>2</sub>O<sub>2</sub> solution and stirred until it dissolves. This solution constitutes the aqueous phase. This phase is then transferred to the 500 cm<sup>3</sup> glass reactor and then the organic phase is added to the aqueous phase. The required amount of phase transfer catalyst (PTC) namely Tetra Butyl Ammonium Bromide (TBAB) (0.0015 gmol) is then added to the reaction mixture and the mixture is stirred at the required temperature (60°C) for 30 minutes.

It was found convenient to analyze the liquid samples from the aqueous phase for their hydrogen peroxide content by 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 after subtracting the amount of hydrogen peroxide decomposed as a result of thermal decomposition at the reaction temperature. The conversion of cyclohexanol was calculated by stoichiometry from the amount of hydrogen peroxide consumed in the reaction.

**3. DEVELOPMENT OF REACTION MECHANISM AND KINETIC MODEL****3.1. Reaction Mechanism**

The reaction mechanism shown in Figure 1 explains a range of experimental findings in the oxidation of alcohols and olefinic compounds [15-18]. In the aqueous phase, the catalyst precursor H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> is rapidly oxidized by H<sub>2</sub>O<sub>2</sub> according to the reaction:



where  $z_1$ ,  $n_1$  and  $n_2$  are stoichiometric coefficients.

The resulting intermediate peroxy species reacts with H<sub>2</sub>O<sub>2</sub> to form the active oxidizing species [AS]<sup>3-</sup>. Then the transfer of the active oxidizing species [AS]<sup>3-</sup> i.e. {PO<sub>4</sub>[W(O)(O<sub>2</sub>)<sub>2</sub>]<sub>4</sub>}<sup>3-</sup>, from the aqueous phase to the organic phase takes place with the help of the phase transfer catalyst Q<sup>+</sup>X<sup>-</sup>:



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 Q<sup>+</sup>. If it is assumed that the simple ion exchange across the interface between organic phase and aqueous phase takes place, then the mechanism of transfer of the active oxidizing species by the quaternary ammonium salt to the organic phase is as shown in Figure 1. A certain amount of halide ion (X<sup>-</sup>) formed in this step is transferred back to the aqueous phase where it could react with the free hydrogen ions (H<sup>+</sup>) generated by the dissociation of the heteropolyacid (viz. H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) to produce HX.

In the organic layer, the active peroxy species reacts with cyclohexanol to form an cyclohexanone, water and the subsequent peroxy species [SPS]<sup>3-</sup>. The subsequent peroxy species is reoxidized by H<sub>2</sub>O<sub>2</sub> after returning to the aqueous phase as the ion pair E. This step may also occur at the organic-aqueous phase interface or even in the organic phase to some extent.

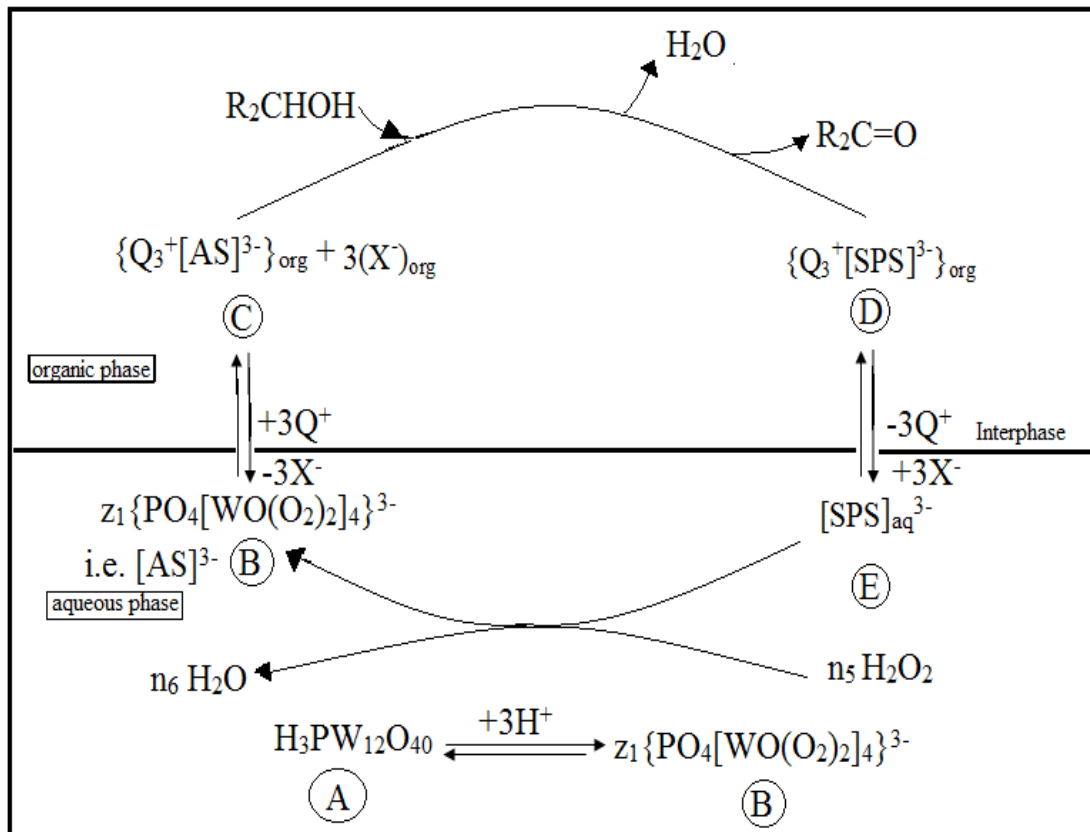


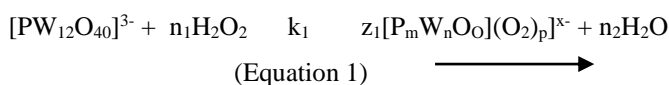
Figure 1 : Reaction Mechanism for Oxidation of Alcohol with H<sub>2</sub>O<sub>2</sub>-HPA-TBAB

### 3.2. Kinetic Model (Theoretical Model or Mathematical Model)

Based on previous studies [15-18], a kinetic model has been proposed for the oxidation of cyclohexanol to cyclohexanone with hydrogen peroxide under synergism of phase transfer catalysis and heteropolyacids. The kinetic model proposed here is valid if the oxidation reaction is assumed to be a phase transfer catalysed reaction carried out under liquid-liquid phase transfer conditions. The following steps are envisaged.

#### Step 1:

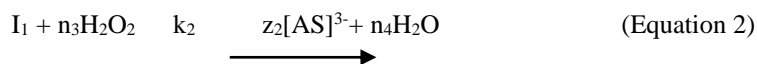
Reaction between the heteropolyacid, e.g. dodeca-tugstophosphoric acid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) in the aqueous phase to generate the intermediate peroxy species I<sub>1</sub>, namely [P<sub>m</sub>W<sub>n</sub>O<sub>6</sub>(O<sub>2</sub>)<sub>p</sub>]<sup>x-</sup>:



where z<sub>1</sub>, n<sub>1</sub> and n<sub>2</sub> are stoichiometric coefficients.

#### Step 2:

Reaction of the intermediate peroxy I<sub>1</sub>, with H<sub>2</sub>O<sub>2</sub> subsequently in the aqueous phase to produce the active oxidizing species [AS]<sup>3-</sup>, namely {PO<sub>4</sub>[W(O)(n<sub>1</sub>H<sub>2</sub>O<sub>2</sub>)<sub>2</sub>]<sub>4</sub>}<sup>3-</sup>:



where  $z_2, n_3$  and  $n_4$  are stoichiometric coefficients.

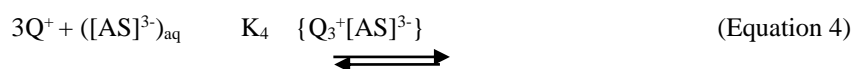
### Step 3:

Dissociation of the phase transfer catalyst in the aqueous phase:



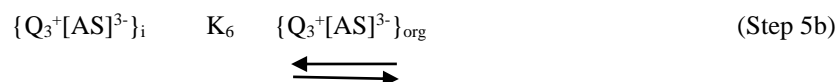
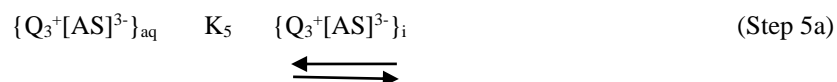
### Step 4:

Formation of the quaternary ammonium pair  $\{Q^+[AS]^{3-}\}$  in the aqueous phase.



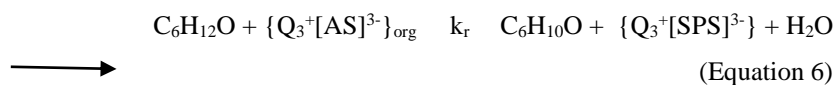
### Step 5:

Transfer of the quaternary ammonium pair  $\{Q_3^+[AS]^{3-}\}$  from the aqueous phase to the interface and then to the organic phase :

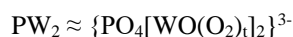
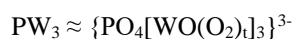
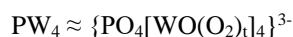


### Step 6:

Reaction between  $\{Q_3^+[AS]^{3-}\}$  and cyclohexanol in the organic phase to form cyclohexanone, water ( $H_2O$ ) and the subsequent peroxy species  $[SPS]^{3-}$ :

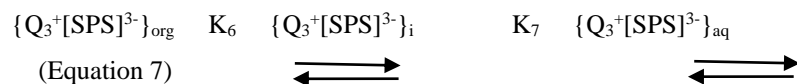


The subsequent peroxy species consists of  $PW_4$ ,  $PW_3$  and  $PW_2$  species which may be inferred to have the following formulae :



### Step 7:

Transfer of the ion pair  $\{Q_3^+[SPS]^{3-}\}$  from the organic phase to the interface and then to the aqueous phase:

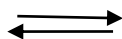


### Step 8:

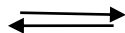
Freeing of the ion pair  $\{Q_3^+[SPS]^{3-}\}$  in the interfacial region:



Step 9:

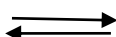


Regeneration of the phase transfer catalyst, i.e. the accessible quaternary ammonium salt in the aqueous phase:



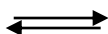
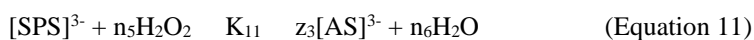
Step 10:

Transfer of water (H<sub>2</sub>O) formed during the reaction from the organic phase to the aqueous phase:



Step 11:

Reaction of the subsequent peroxy species (SPS) with H<sub>2</sub>O<sub>2</sub> in the aqueous phase to regenerate the active oxidising species [AS]<sup>3-</sup>:



where  $z_3$ ,  $n_5$  and  $n_6$  are stoichiometric coefficients.

In the above equations,  $k_1$ ,  $k_2$  and  $k_r$  are reaction rate constants while  $K_3$ ,  $K_4$ ,  $K_5$ ,  $K_6$ ,  $K_7$ ,  $K_8$ ,  $K_9$ ,  $K_C$ ,  $K_{10}$  and  $K_{11}$  the equilibrium constants. Since the rates of steps 1, 2, 3, 4, 6, 7, 8, 9, 10 and 11 are assumed to be much greater than the rate of step 5 if the reaction is mass transfer controlled, these steps may be neglected while developing a suitable mathematical model. Since step 5a may also be assumed to be a fast step, the relevant step to be considered is step 5b. At steady state, the following rate equations may be written for step 5b of the proposed theoretical model which is based on the two film theory of mass transfer:

**For step 5b:**

Rate of transfer of  $\{Q_3^+[AS]^{3-}\}$  from the interface to the organic phase may be written as:

$$R_{c\bar{a}} = k_{LC\bar{a}} (\{Q_3^+[AS]^{3-}\}_{org,i} - \{Q_3^+[AS]^{3-}\}_{org,b}) \quad \text{(Equation 12)}$$

where  $R_{c\bar{a}}$  = volumetric rate of transfer of  $\{Q_3^+[AS]^{3-}\}$  from the interface to the bulk organic phase.

$k_{LC\bar{a}}$  = mass transfer coefficient for transfer of  $\{Q_3^+[AS]^{3-}\}$  from the interface to the bulk organic phase.

$\bar{a}$  = interfacial area per unit volume of the organic phase.

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

If the reaction systems conforms to the slow reaction regime (Regime 2) as shown in Figure 2, then there will be no free  $\{Q_3^+[AS]^{3-}\}$  present in the bulk organic phase i.e.  $\{Q_3^+[AS]^{3-}\}_{org,b} = 0$  and the following rate equation will be valid:

$$R_{c\bar{a}} = k_{LC\bar{a}} \{Q_3^+[AS]^{3-}\}_{org,i} \quad \text{(Equation 13)}$$

The rate of reaction is independent of the concentration of cyclohexanol and the reaction is zero order with respect to the concentration of cyclohexanol.

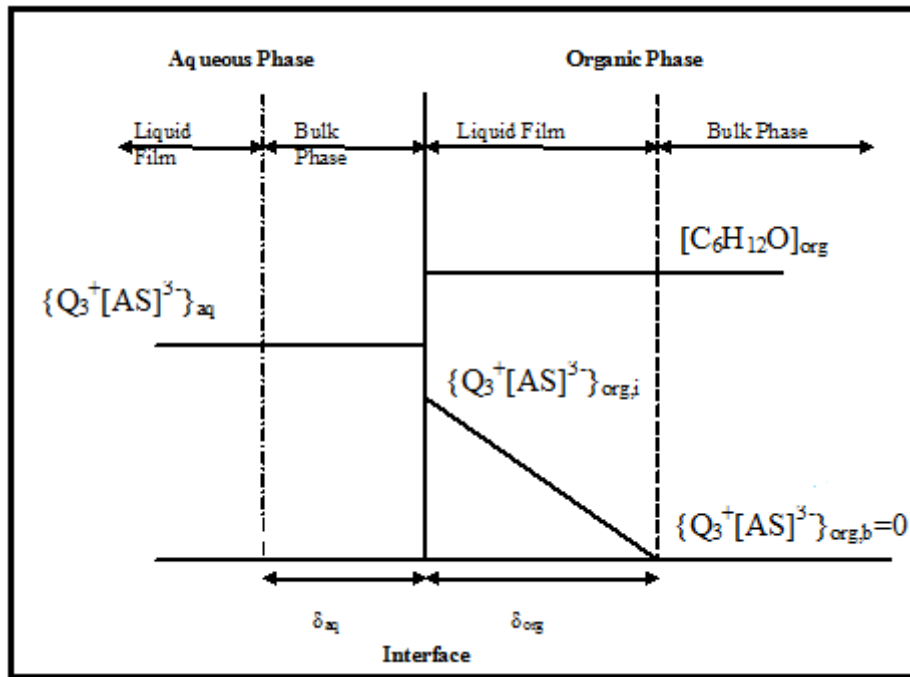


Figure 2: Typical Concentration Profile for Regime 2 (Slow Reaction)

**in Liquid-Liquid Phase Transfer Catalyzed Oxidation of Cyclohexanol**

( $\delta_{aq}$  = Thickness of aqueous phase film next to interface,  $\delta_{org}$  = Thickness of organic phase film next to interface. Two film theory of mass transfer is assumed to be valid.)

It is to be noted, however, that the concentration of cyclohexanol does not drop appreciably within the film in the organic phase during the reaction and hence in this case:

$$[C_6H_{12}O]_{org,i} = [C_6H_{12}O]_{org,b} = [C_6H_{12}O]_{org} \quad \text{(Equation 14)}$$

If it is assumed that the active oxidizing species  $[AS]^{3-}$  is the dominant polytungstophosphate present under steady state turnover conditions (biphasic with aqueous hydrogen peroxide present), then the expression for the total concentration of the phase transfer catalyst in the organic phase ( $Q_o$ ) may be written as

$$Q_o = [Q^+X^-]_o + [Q_3^+AS^{3-}]_o \quad \text{(Equation 15)}$$

Under the given experimental conditions (viz. a well-stirred mixture), it may be assumed that the phase transfer catalyst will exist in the organic phase as  $\{Q_3^+AS^{3-}\}$  and  $\{Q^+X^-\}$  in constant proportion. This implies that:

$$\frac{[Q_3^+AS^{3-}]_o}{[Q^+X^-]_o} = \text{CONSTANT} = \phi \quad \text{(Equation 16)}$$

Equation 16 can be substituted in Equation 15 to give the expression:

$$[Q_3^+AS^{3-}]_o = \frac{\phi Q_o}{(1 + \phi)} \quad \text{(Equation 17)}$$

Using Equation 16 in the Equation 13 gives :

$$R_{c\bar{a}} = k_{LC\bar{a}} \phi Q_o / (1 + \phi) \quad \text{(Equation 18)}$$

Equation 18 suggests that the reaction is first-order with respect to the total concentration of the phase transfer catalyst in the organic phase.

Since the rate of the reaction varies linearly with  $\{Q_3^+[AS]^{3-}\}_{org,i}$  as seen from Equation 13 it follows from the theoretical model that the rate of reaction should also vary linearly with the concentration of hydrogen peroxide in the aqueous phase and also vary linearly with the concentration of phosphotungstic acid (co-catalyst) in the aqueous phase.

The validity of the proposed mathematical (theoretical) model was tested by studying experimentally the effect of various parameters such as speed of agitation, temperature, concentration of cyclohexanol, concentration of oxidizing agent namely hydrogen peroxide ( $H_2O_2$ ), concentration of phase transfer catalyst and co-catalyst loading on the rate of reaction. The observed experimental results which are discussed in the following section could be satisfactorily explained with the help of the proposed model.

### 3. RESULTS AND DISCUSSION

#### 4.

The Liquid-Liquid Phase Transfer Catalyzed (L-L PTC) oxidation of cyclohexanol was carried out with hydrogen peroxide as an oxidizing agent and with tetra butyl ammonium bromide (TBAB) as the phase transfer catalyst and phosphotungstic acid ( $H_3PW_{12}O_{40}$ ) as the co-catalyst. It was observed that the reaction takes place to a significant extent (89% conversion) in 30 minutes at a temperature of  $60^\circ C$  and a speed of agitation of 1200 rpm. As hydrogen peroxide was used in stoichiometric amount or as the limiting reactant in almost all of the experiments it is presumed that the only products formed in the oxidation reaction are cyclohexanone and water and over-oxidation to adipic acid is minimized.

Thus, it was decided to study the effect of different parameters such as speed of agitation, temperature, concentration of cyclohexanol, concentration of  $H_2O_2$ , phase transfer catalyst concentration and co-catalyst loading on the rate of reaction for this liquid-liquid phase transfer catalytic oxidation system.

#### 4.1. Effect of Speed of Agitation

To ascertain the influence of mass transfer limitations in the L-L PTC oxidation of cyclohexanol with oxidizing agent  $H_2O_2$ , the speed of agitation was varied in the range of 1200–2000 rpm under otherwise similar conditions (namely, 0.088 gmol cyclohexanol, organic phase made up to 100 ml with ethyl acetate as solvent, aqueous phase (30% w/v  $H_2O_2$ ) volume = 50 ml, 0.0005 gmol of phosphotungstic acid, 0.0015 gmol of PTC (TBAB) loading, temperature = 333K).

The effect of speed of agitation on the rate of reaction was studied and it was found that the rate of reaction was found to be independent of the speed of agitation at speed of agitation above 1200 rpm as shown in Figure 3.

The experimental results obtained indicate that the oxidation reaction is kinetically controlled and mass transfer effects may not be significant at speed of agitation above 1200 rpm. However, to study the influence of mass transfer limitations in this reaction which could become important in the industrial scale process a speed of agitation of 1200 rpm was used while studying the effect of other parameters on the rate of reaction.

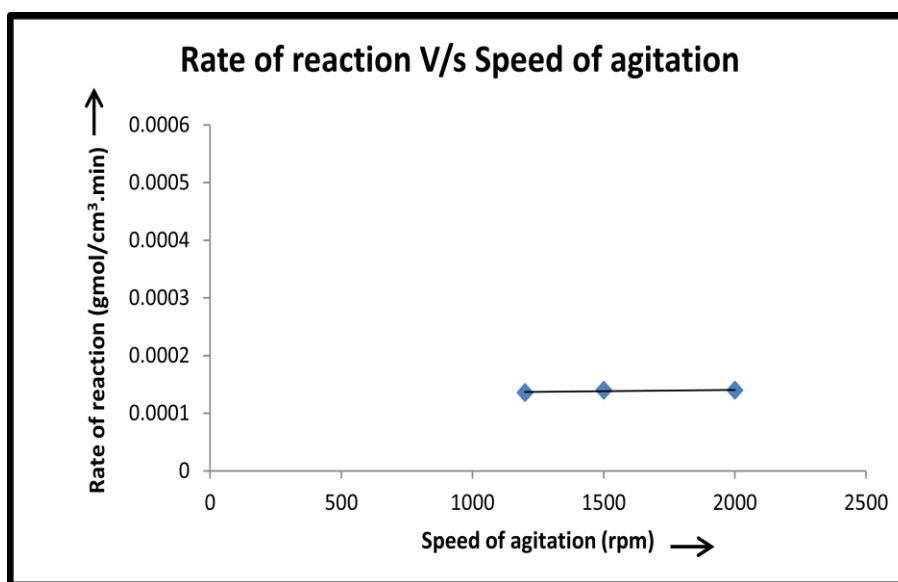


Figure 3: Rate of Reaction V/s Speed of agitation

(0.088gmol cyclohexanol, organic phase made up to 100 ml with ethyl acetate as solvent, aqueous phase (30% w/v  $H_2O_2$ ) volume = 50 ml, 0.0005 gmol of phosphotungstic acid, 0.0015 gmol of PTC (TBAB) loading, temperature = 333K)

#### 4.2. Effect of Temperature

The effect of temperature on the oxidation of cyclohexanol was studied by varying the temperature from 40°C (313K) to 60°C (333K) under otherwise similar conditions (0.088 gmol cyclohexanol, organic phase made up to 100 ml with ethyl acetate as solvent, aqueous phase (30% w/v  $H_2O_2$ ) volume = 50 ml, 0.0005 gmol of phosphotungstic acid, 0.0015 gmol of PTC (TBAB) loading, speed of agitation = 1200 rpm). Higher reaction temperatures were not used since thermal decomposition of hydrogen peroxide may be significant at temperatures of 70°C and above.

The calculated activation energy from the Arrhenius plot for the temperature range of 40°C-60°C using initial rate of reaction is 1.48 kcal/gmol (Figure 4), which indicates that the reaction may be mass transfer controlled.

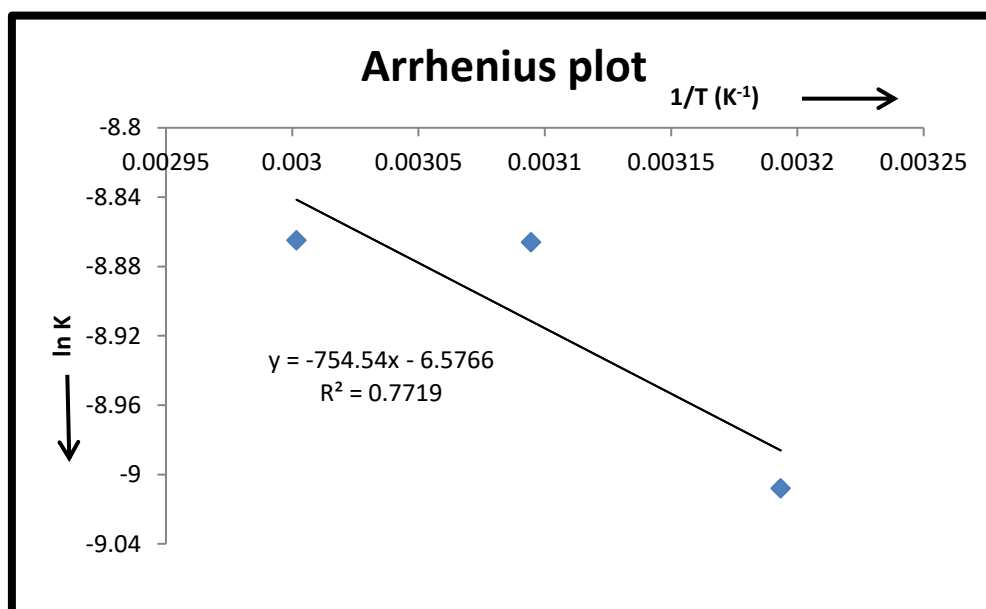


Figure 4: Arrhenius Plot

(0.088gmol cyclohexanol, organic phase made up to 100 ml with ethyl acetate as solvent, aqueous phase (30% w/v  $H_2O_2$ ) volume = 50 ml, 0.0005 gmol of phosphotungstic acid, 0.0015 gmol of PTC (TBAB) loading, speed of agitation = 1200 rpm)

#### 4.3. Effect of Concentration of Cyclohexanol

The effect of concentration of cyclohexanol in the organic phase on the oxidation reaction was studied by varying the concentration of cyclohexanol in the organic phase from 0.00088 gmol/cm<sup>3</sup> to 0.00176 gmol/cm<sup>3</sup> under otherwise similar conditions (namely, organic phase made up to 100 ml with ethyl acetate as solvent, aqueous phase (30% w/v  $H_2O_2$ ) volume = 50 ml, 0.0005 gmol of phosphotungstic acid, 0.0015 gmol of PTC (TBAB) loading, speed of agitation = 1200 rpm, temperature = 333K).

A plot of initial rate of reaction versus concentration of the cyclohexanol in the organic phase was prepared as shown in Figure 5 and it was observed that the initial rate of reaction was independent of the concentration of cyclohexanol in the organic phase for the concentration range studied. This shows that the reaction is zero order with respect to the concentration of cyclohexanol. This suggests that the reaction may be mass transfer controlled.



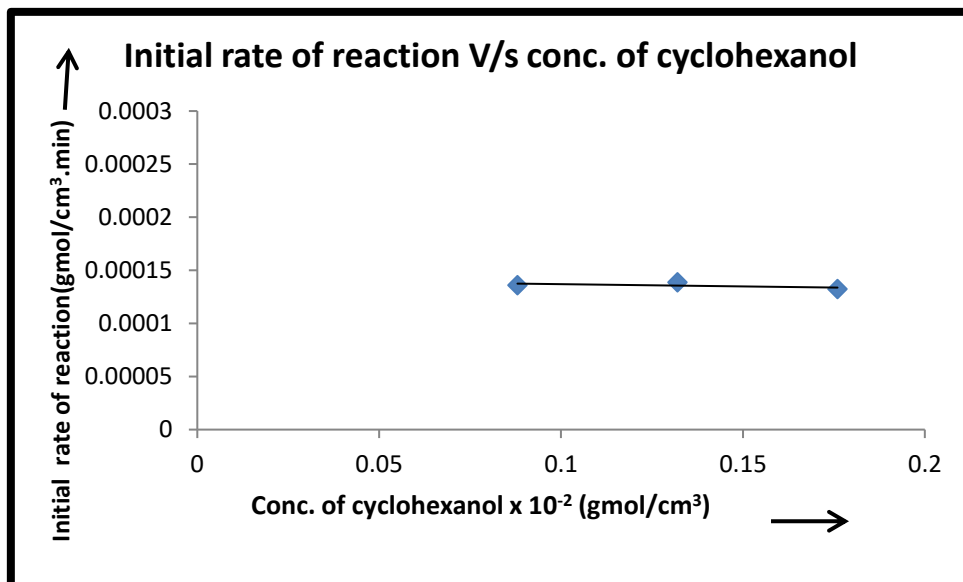


Figure 5: Initial Rate of Reaction V/s Concentration of Cyclohexanol

(Volume of organic phase made up to 100 ml with ethyl acetate as solvent, volume of aqueous phase (30% w/v H<sub>2</sub>O<sub>2</sub>) volume = 50 ml, 0.0005 gmol of phosphotungstic acid, 0.0015 gmol of PTC (TBAB) loading, speed of agitation = 1200 rpm, temperature = 333K)

#### 4.4. 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 0.0044 gmol/cm<sup>3</sup> to 0.0132 gmol/cm<sup>3</sup> under otherwise similar conditions (namely, 0.088 gmol cyclohexanol, organic phase made up to 100 ml with ethyl acetate as solvent, aqueous phase (30% w/v H<sub>2</sub>O<sub>2</sub>) volume = 50 ml, 0.0015 gmol of PTC (TBAB) loading, speed of agitation = 1200 rpm, temperature = 333K).

A plot of initial rate of reaction versus concentration of hydrogen peroxide in the aqueous phase was prepared as shown in Figure 6 and it was observed that the initial rate of reaction was linearly dependent on the concentration of hydrogen peroxide in the aqueous phase for the concentration range studied. This shows that the reaction is first order with respect to the concentration of hydrogen peroxide in the aqueous phase.

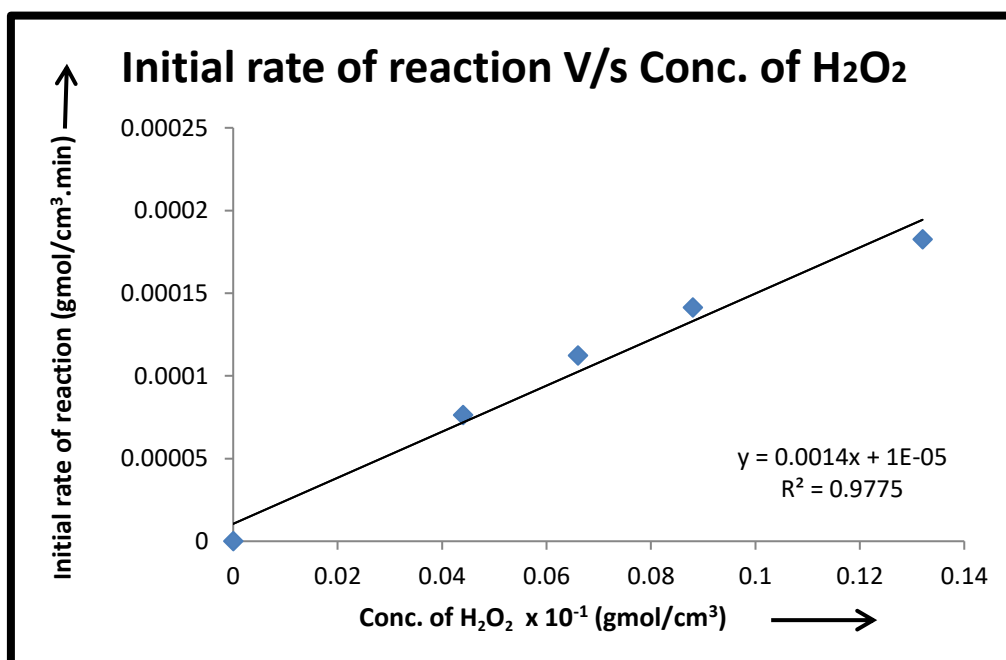


Figure 6: Initial Rate of Reaction V/s Concentration of H<sub>2</sub>O<sub>2</sub>

(0.088 gmol cyclohexanol, volume of organic phase made up to 100 ml with ethyl acetate as solvent, volume of aqueous phase (30% w/v H<sub>2</sub>O<sub>2</sub>) = 50 ml, 0.0015 gmol of PTC [TBAB] loading based on cyclohexanol, temperature = 333K, speed of agitation = 1200 rpm)

#### 4.5. Effect of Concentration of Phase Transfer Catalyst

The effect of concentration of phase transfer catalyst on the oxidation of cyclohexanol was studied by varying the phase transfer catalyst (tetra butyl ammonium bromide, TBAB) concentration from 0.000005 gmol/cm<sup>3</sup> to 0.00002 gmol/cm<sup>3</sup> under otherwise similar conditions (namely, 0.088 gmol cyclohexanol, organic phase made up to 100 ml with ethyl acetate as solvent, aqueous phase (30% w/v H<sub>2</sub>O<sub>2</sub>) volume = 50 ml, 0.0005 gmol phosphotungstic acid, speed of agitation = 1200 rpm, temperature = 333K).

A plot of initial rate of reaction versus total concentration of the phase transfer catalyst in the organic phase was prepared as shown in Figure 7 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. It was also observed from this plot that the reaction may also take place to some extent in the absence of the phase transfer catalyst.

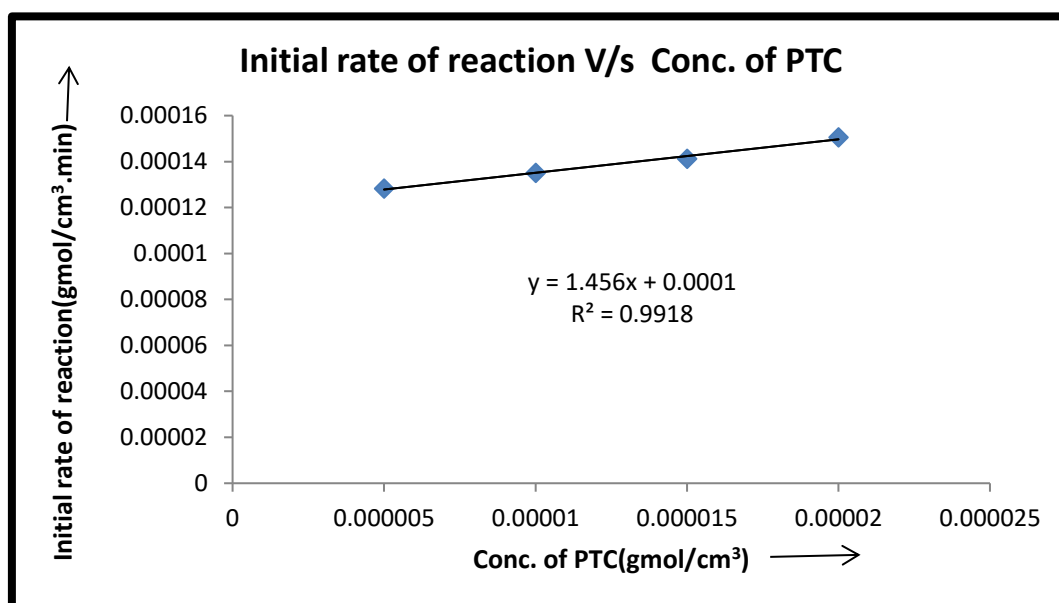


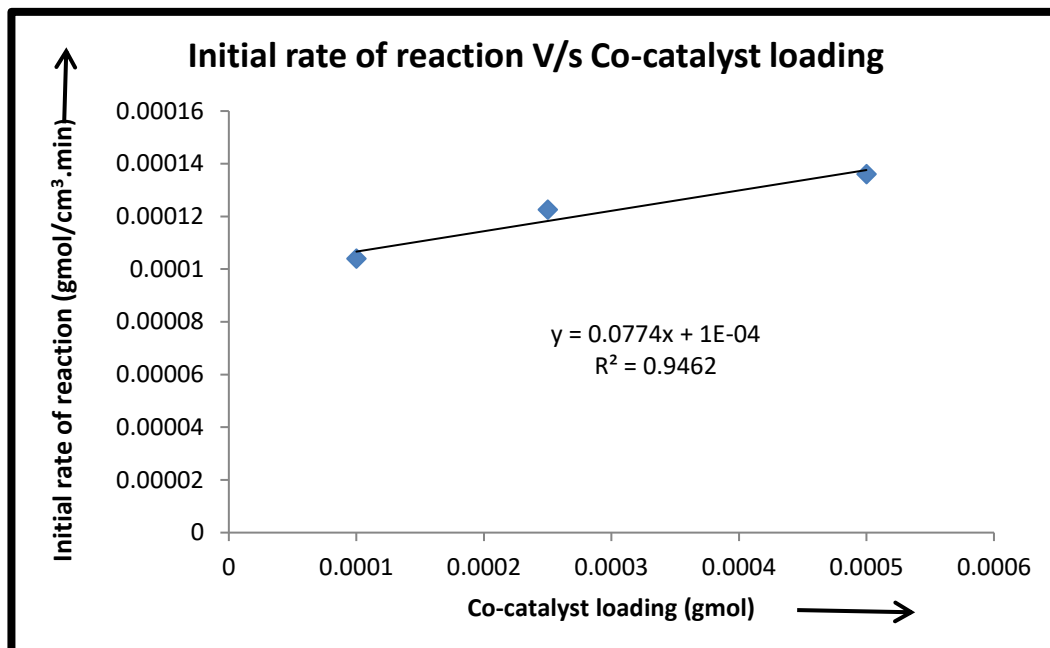
Figure 7: Initial Rate of Reaction V/s Total Concentration of PTC

(0.088 gmol cyclohexanol, volume of organic phase made up to 100 ml with ethyl acetate as solvent, volume of aqueous phase (30% w/v H<sub>2</sub>O<sub>2</sub>) = 50 ml, 0.0005 gmol of phosphotungstic acid, temperature = 333K, speed of agitation = 1200 rpm)

#### 4.6. Effect of Co-Catalyst Loading

The effect of co-catalyst loading on the oxidation of cyclohexanol was studied by varying the co-catalyst (phosphotungstic acid, H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) loading from 0.0001 gmol to 0.0005 gmol (based on cyclohexanol) under otherwise similar conditions (namely, 0.088 gmol cyclohexanol, organic phase made up to 100 ml with ethyl acetate as solvent, aqueous phase (30% w/v H<sub>2</sub>O<sub>2</sub>) volume = 50 ml, 0.0015 gmol of phase transfer catalyst, speed of agitation = 1200 rpm, temperature = 333K).

A plot of initial rate of reaction versus co-catalyst loading was prepared as shown in Figure 8 and it was observed that the initial rate of reaction was linearly dependent on the co-catalyst loading. This implies that the reaction is first order with respect to the concentration of co-catalyst in the aqueous phase. It was also observed from this plot that the reaction may also take place to some extent in the absence of the co-catalyst.



**Figure 8: Initial Rate of Reaction V/s Co-catalyst Loading**

(0.088 gmol cyclohexanol, volume of organic phase made up to 100 ml with ethyl acetate as solvent, volume of aqueous phase (30% w/v H<sub>2</sub>O<sub>2</sub>) = 50 ml, 0.0015 gmol of PTC (TBAB) loading based on cyclohexanol, temperature = 333K, speed of agitation = 1200 rpm)

## 5. CONCLUSION

The rate of oxidation of cyclohexanol to cyclohexanone with hydrogen peroxide was found to be enhanced by the use of a phase transfer catalyst and a heteropolyacid such as dodeca-tungstophosphoric acid (phosphotungstic acid) as co-catalyst. The experimental results suggest that the rate of reaction is dependent on the speed of agitation at speeds less than 1200 rpm. The calculated activation energy from the Arrhenius plot for the temperature range of 40<sup>o</sup>C-60<sup>o</sup>C using initial rate of reaction is 1.48 kcal/gmol, which indicates that the reaction may be mass transfer controlled. The initial rate of reaction was independent on the concentration of cyclohexanol in the organic phase for the concentration range studied. The initial rate of reaction was found to be linearly dependent on the concentration of hydrogen peroxide in the aqueous phase, the total concentration of the phase transfer catalyst in the organic phase and the co-catalyst loading. The experimental results are in agreement with the proposed reaction mechanism and kinetic model.

## CONFLICT OF INTEREST

The authors declare no conflict of interest.

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