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Kinetics of Liquid-Liquid Phase Transfer Catalyzed Green Oxidation of Cyclohexanol to Cyclohexanone with Hydrogen Peroxide

D.A. More[1], S.V. Ranade[2], C.K. Mistry[3]*

Department of Chemical Engineering, Mahatma Gandhi Mission's College of Engineering and Technology, Kamothe, Navi Mumbai- 410209, Maharashtra, India[1-3]

*Corresponding Author

Abstract: The oxidation of organic compounds is an important and widely used reaction in laboratory scale organic synthesis as well as in large scale chemical industrial processes. The catalytic oxidation with hydrogen peroxide (H_2O_2) in aqueous solutions offers an economic and environmentally friendly or green alternative for oxidation reactions. The oxidation of cyclohexanol plays an important role in organic synthesis and the desired product namely cyclohexanone is widely used as an intermediate in the production of both adipic acid (for use in nylon 66) and caprolactum (monomer for nylon 6). Over 96% of all cyclohexanone produced is either oxidized to adipic acid or converted to cyclohexanone oxime, which is then rearranges with sulphuric acid to caprolactum. Cyclohexanone is used as a thinner or solvent for synthetic resins, polymers and lacquers. It is also used as starting material in the synthesis of many insecticides, herbicides and pharmaceuticals.

Phase transfer catalysis (PTC) is an attractive technique for synthesis of organic chemicals from two immiscible reactants existing in two different phases, which otherwise normally cannot react with each other due to their low mutual solubility in other phase and hence their low interaction. In this research work tetra butyl ammonium bromide (TBAB) was used as a phase transfer catalyst along with sodium tungstate as a co-catalyst in the oxidation of cyclohexanol to cyclohexanone with hydrogen peroxide and the effects of various reaction parameters were studied. A kinetic model for the oxidation reaction was developed based on the experimental results.

Keywords: Cyclohexanone, Green Oxidation, Phase Transfer Catalysis, Hydrogen Peroxide, Sodium Tungstate, Kinetic Model.

INTRODUCTION

The oxidation of primary and secondary alcohols to aldehydes and ketones is one of the most important transformations in organic chemistry both at a laboratory and industrial scale [1].

The catalytic oxidation with hydrogen peroxide (H_2O_2) in aqueous solutions offers an economic and environmentally safe alternative for oxidation reactions performed in synthetic laboratories and chemical industry. Applications where oxidation reactions are required are diverse, ranging from pulp and textile bleaching to production of fine chemicals. At the moment, most of these processes are carried out by using stoichiometric oxidants, such as peroxides, chlorine-bearing compounds and high valent transition metal oxides.

The oxidation of cyclohexanol plays an important role in organic synthesis [1] and the desired product namely cyclohexanone is widely used as an intermediate in the production of both adipic acid (for use in nylon 66) and caprolactum (monomer for nylon 6). Over 96% of all cyclohexanone produced is either oxidized to adipic acid or converted to cyclohexanone oxime, which is then rearranges with sulphuric acid to caprolactum. Cyclohexanone is used as a thinner or solvent for synthetic resins, polymers and lacquers. It is also used as starting material in the synthesis of many insecticides, herbicides and pharmaceuticals.

It is proposed to study the catalytic oxidation of cyclohexanol to cyclohexanone with hydrogen peroxide in this research work.

The transformation of alcohols into aldehydes or ketones is a fundamental reaction in organic synthesis. A number of methods are known for alcohol oxidation. However, the development of newer methods and methodologies is gaining

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much attention currently due to the significance of this reaction. Alcohol oxidation reactions with stoichiometric amounts of dichromate and permanganate of the previous century are being replaced by modern methods involving catalytic amounts of metal catalysts in combination with oxidants such as dioxygen or hydrogen peroxide. The utilization of the hydrogen peroxide as an oxidant for organic substrates has gained much attention in recent years, because of its environmental implications, water being the only by-product formed. These oxidation reactions offer the advantages of simple processes, easy work-up, low cost and reduction in noxious waste materials. A series of catalytic systems for the hydrogen peroxide-based oxidation of alcohols to aldehydes have been reported [2].

Phase transfer catalysis (PTC) is an attractive technique for synthesis of organic chemicals from two immiscible reactants existing in two different phases, which otherwise normally cannot react with each other due to their low mutual solubility in other phase and hence their low interaction [3,4]. In PTC, reaction is brought about by use of small quantities of an agent which transfers one reactant across the interface into the other phase so that the reaction can proceed. The phase transfer agent is not consumed but performs the transport function repeatedly.

The kinetics of the oxidation cyclohexanol to cyclohexanone with hydrogen peroxide under liquid-liquid phase transfer catalysis in which the reactants are in two separate phases (namely the organic and aqueous phases) were investigated. The effect of various parameters such as speed of agitation, temperature, concentration of cyclohexanol, concentration of H_2O_2, phase transfer catalyst (tetra butyl ammonium bromide, TBAB) loading, and co-catalyst (sodium tungstate) loading rate of reaction were studied. A mechanism for the reaction was proposed and a mathematical model was developed for the environmentally friendly catalytic oxidation system.

EXPERIMENTAL SECTION

Chemicals and Catalysts:

Cyclohexanol of AR grade was obtained from M/s s.d. Fine Chemicals Pvt. Ltd, Mumbai, India. Hydrogen Peroxide (H_2O_2 - 30% w/v Solution), Sodium Tungstate ($Na_2WO_4.2H_2O$), Ethyl Acetate and Tetra Butyl Ammonium Bromide (TBAB) of 99.5% purity were obtained from M/s Merck Specialities Pvt. Ltd, Mumbai, India.

Experimental Procedure:

The oxidation of cyclohexanol with hydrogen peroxide was carried out batchwise in a fully baffled mechanically agitated glass reactor of capacity 500 cm^3 (6.5 cm i.d.). A 2.0 cm-diameter three-bladed glass pitched turbine impeller with the provision of speed regulation, located at a height of 1.5 cm from the bottom, was used for stirring the reaction mixture. The reactor was kept in a constant temperature water bath whose temperature could be controlled within ±1°C. A reflux condenser was attached to the reactor when the experiments were carried out at temperatures above 60^0C.

Typical liquid-liquid PTC reactions were conducted by taking 0.44 gmol cyclohexanol and adding ethyl acetate as solvent until the total volume of the organic phase was 100 ml (using a 100 ml standardization volumetric flask). Then the required amount of sodium tungstate (0.0025 gmol) was added to 50 ml of 30 % w/v H_2O_2 solution (0.44 gmol of H_2O_2) and stirred until it dissolved completely. This solution constituted the aqueous phase. The aqueous phase was then added to the 500 cm^3 glass reactor and then the organic phase was transferred to the aqueous phase in the reactor. All the experiments were carried out using an organic phase to aqueous phase volume ratio of 2. 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 1000 rpm with the temperature maintained at 60^0C for the desired time period (30 min.).

ANALYTICAL TECHNIQUES

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.

MECHANISM OF REACTION AND KINETIC MODEL

Reaction Mechanism:

The mechanism shown in Scheme 1 explains a range of experimental findings in the oxidation of alcohols, ketones and olefins [5-10]. In an aqueous phase, the catalyst precursor Na_2WO_4 is rapidly oxidized by H_2O_2 according to the reaction:

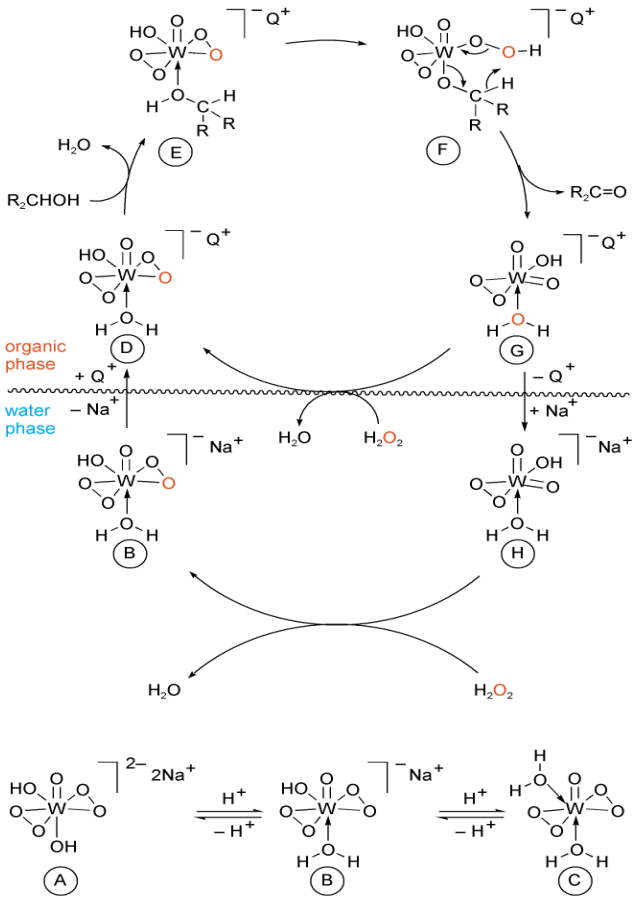
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$Na_2WO_4 + 2H_2O_2 \rightarrow Na_2[WO(O_2)_2(OH)_2] + H_2O$. The resulting bisperoxotungstate compound **A** is in equilibrium with **B** and **C**. The dianion in **A** is feebly active toward alcohols, while the mono- and di-protonated forms in **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 HSO_4^- ion is largely deprotonated to 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 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 a ketonic product and **G**. 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. This view is supported by the relative reactivity of *p*-substituted benzyl alcohols (< 10% conversion) showing a ρ value of -0.31. The monoperoxo tungstate ion in **G** is reoxidized by H_2O_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. H_2WO_4, 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.



Scheme 1: Catalytic Cycle of Alcohol Oxidation using PTC-H_2O_2-$Na_2WO_4.2H_2O$ system.

Based on the reaction mechanism described above, the following steps are assumed to take place in the liquid-liquid phase transfer catalysed (L-L PTC) oxidation of cyclohexanol to cyclohexanone using hydrogen peroxide as the oxidising agent and sodium tungstate as the co-catalyst:

Step 1:

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

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

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Step 2:
Formation of the mono-protonated form of the bisperoxotungstate compound in the aqueous phase:

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

Step 3:
Dissociation of the phase transfer catalyst (Tetrabutyl Ammonium Bromide, TBAB) in the aqueous phase:

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

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

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

Step 4:
Formation of the quaternary ammonium pair $\{Q^+[WO(O_2)_2(OH)(H_2O)]^-\}$ in the aqueous phase by Na^+-Q^+ ion exchange:

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

Step 5:
Transfer of the quaternary ammonium pair $\{Q^+[WO(O_2)_2(OH)(H_2O)]^-\}$ from the aqueous phase to the organic phase:

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

where the subscripts aq and org denote the aqueous phase and organic phase, respectively.

Step 6:
Reaction between the quaternary ammonium pair $\{Q^+[WO(O_2)_2(OH)(H2O)]^-\}$ and cyclohexanol in the organic phase:

$$\{Q^+[WO(O_2)_2(OH)(H_2O)]^-\}_{org} + C_6H_{11}OH \rightarrow C_6H_{10}O + \{Q^+[WOO(O_2)(OH)(H_2O)]^-\}org + H_2O\}$$

Step 7:
Transfer of the quaternary ammonium pair $\{Q^+[WOO(O_2)(OH)(H_2O)]^-\}$ from the organic phase to the aqueous phase:

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

Step 8:
Formation of the monoperoxotungstate compound $Na^+[WOO(O_2)(OH)(H_2O)]^-$ in the aqueous phase by Na^+-Q^+ ion exchange:

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

Step 9:
Oxidation of the monoperoxotungstate compound $Na^+[WOO(O_2)(OH)(H_2O)]^-$ in the aqueous phase by hydrogen peroxide:

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

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

Kinetic Model (Mathematical Model)
Mathematical modeling of liquid-liquid phase transfer catalyzed oxidation reactions has been reported by some researchers [11-18]. It is assumed in the present case that steps 1,2,3,4,5,7,8 and 9 are fast compared to step 6 which is the slowest step and hence the rate controlling step.

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

$$r = -d[C_6H_{11}OH]/dt = k[Q^+[WO(O_2)_2(OH)(H_2O)]^-]_{org}[C_6H_{11}OH]_{org} \quad \text{(Equation 1)}$$

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where r denotes the intrinsic rate of chemical reaction of cyclohexanol to cyclohexanone in the organic phase.

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

$$[Q_t] = [Q^+[WO(O_2)_2(OH)(H_2O)]^-]_{org} + [Q^+[WOO(O_2)(OH)(H_2O)^-]_{org} + ([Q^+[WO(O_2)_2(OH)(H_2O)^-]]_{aq} + [Q^+[WOO(O_2)(OH)(H_2O)]^-]_{aq} + [Q^+]_{aq}) V_{aq}/V_{org} \quad \text{(Equation 2)}$$

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

The following equilibrium relationships are valid:

$$K_1 = [Q^+[AS]^-]_{org} / [Q^+[AS]^-]_{aq} \quad \text{(Equation 3)}$$

$$K_2 = [Q^+[SPS]^-]_{org} / [Q^+[SPS]^-]_{aq} \quad \text{(Equation 4)}$$

Therefore, we can write:

$$[Q^+[AS]^-]_{aq} = [Q^+[AS]^-]_{org} / K_1 \quad \text{(Equation5)}$$

$$[Q^+[SPS]^-]_{aq} = [Q^+[SPS]^-]_{org} / K_2 \quad \text{(Equation6)}$$

Substituting the values of $[Q^+[AS]^-]_{aq}$ and $[Q^+[SPS]^-]_{aq}$ from equations 5 and 6 in equation 2 gives:

$$[Q_t] = [Q^+[AS]^-]_{org} + [Q^+[SPS]^-]_{org} + (([Q^+[AS]^-]_{org} /K_1) + ([Q^+[SPS]^-]_{org}/K_2) + [Q^+]_{aq})V_{aq}/ V_{org} \quad \text{(Equation 7)}$$

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

Therefore, Equation 7 may be written as :

$$[Q_t] = ((1+(1/K_1)(V_{aq}/V_{org}))[Q^+[AS^-]]_{org} + ((1+(1/K_2)(V_{aq}/V_{org}))[Q^+[SPS^-]]_{org} \quad \text{(Equation 8)}$$

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

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

Therefore Equation 8 may be written as:

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

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

$$[Q_t] = ((1+(1/K_1)(1/V_r))[Q^+[AS]^-]_{org} \quad \text{(Equation 10)}$$

$$[Q_t] = ((K_1V_r+1)/K_1Vr)[Q^+[AS]^-]_{org} \quad \text{(Equation 11)}$$

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

$$[Q^+[AS]^-]_{org} = \varphi\ [Q_t] \quad \text{(Equation 13)}$$

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

Substituting the value of $[Q^+[AS]^-]_{org}$ from Equation 13 in Equation 1 gives :

$$r = k\ \varphi\ [Q_t][C_6H_{11}OH]_{org} \quad \text{(Equation 14)}$$

Now, from Equation 3:

$$[Q^+[AS]^-]_{org} = K_1\ [Q^+[AS]^-]_{aq} \quad \text{(Equation 15)}$$

Substituting the value of $[Q^+[AS]^-]_{org}$ from Equation 15 in Equation 11 gives :

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$[Q_t] = ((K_1V_r+1)/K_1V_r)K_1[Q^+[AS]^-]_{aq}$ (Equation 16)

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

The following equilibrium relationships are also valid:

$K_3 = [Q^+[AS]^-]_{aq}[Na^+]_{aq} / [Q^+]_{aq}[Na^+[AS]^-]_{aq}$ (Equation 18)

$K_4 = [Na^+[AS]^-]_{aq}[Na^+]_{aq}/[Na_2[WO(O_2)_2(OH)_2]]_{aq}[H^+]_{aq}$ (Equation 19)

$K_5 = [Na_2[WO(O_2)_2(OH)_2]]_{aq}[H_2O]_{aq} / [Na_2WO_4]_{aq}[H_2O_2]^2_{aq}$ (Equation 20)

Using Equations 18, 19 and 20 in Equation 17 gives:

$[Q_t] = K_1K_3K_4K_5[Na_2WO_4]_{aq}[H_2O_2]^2_{aq}[H^+]_{aq} / \varphi\ [Na^+]^2_{aq}[H_2O]_{aq}$ (Equation 21)

From Equation 21 it is observed that $[Q_t]$ varies linearly with $[Na_2WO_4]_{aq}$ and from Equation 14 it is observed that the rate of reaction r varies linearly with $[Q_t]$, therefore it may be concluded that r varies linearly with $[Na_2WO_4]_{aq}$ and the reaction should be first order with respect to the concentration of sodium tungstate, Na_2WO_4.

The validity of the proposed kinetic (mathematical) model was tested by studying experimentally the effect of various parameters such as speed of agitation, temperature, concentration of cyclohexanol, concentration of oxidising agent namely hydrogen peroxide (H_2O_2), concentration of phase transfer catalyst and concentration of co-catalyst namely sodium tungstate (Na_2WO_4) on the conversion of cyclohexanol and the rate of reaction. The observed experimental results when H_2O_2 was used as the oxidising agent (which are discussed in the following sections) could be satisfactorily explained with the help of the proposed model.

EFFECT OF DIFFERENT PARAMETERS

To validate the proposed mechanism, effects of various parameters on the rate of reaction were studied. All the reactions were carried out for the period of 30 min.

Effect of Speed of Agitation:

To ascertain the influence of mass transfer limitations in the L-L PTC oxidation of cyclohexanol with H_2O_2, the speed of agitation was varied in the range of 500–1500 rpm under otherwise similar conditions (namely, 0.44 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, 0.0025 gmol of sodium tungstate, 0.005 gmol of PTC (TBAB) loading, temperature = 333K). The effect of speed of agitation on the initial rate of reaction was studied and it was found that the initial rate of reaction was found to independent of the speed of agitation as shown in Figure 1. This shows that mass transfer effects are negligible in this oxidation reaction. The experimental results obtained indicate that the oxidation reaction is kinetically controlled.

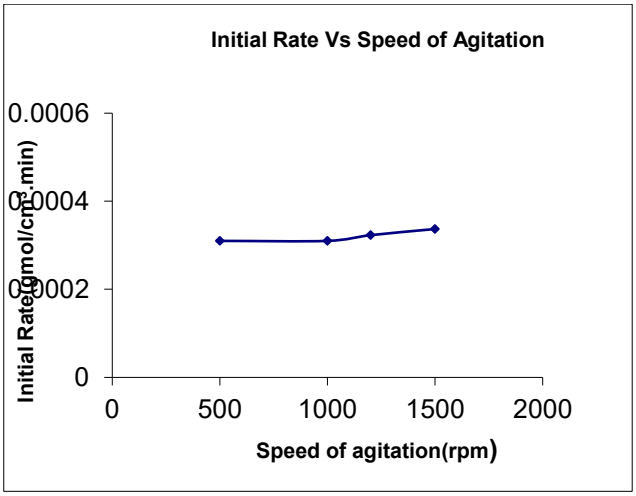


Figure 1: Initial Rate of Reaction v/s Speed of Agitation

Effect of Temperature:

The effect of temperature on the oxidation of cyclohexanol was studied by varying the temperature from 40^0C (313K) to 60^0C (333K) under otherwise similar conditions (namely, 0.44 gmol cyclohexanol, organic phase made up to 100 ml with

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ethyl acetate as solvent, aqueous phase (30% w/v H_2O_2) volume = 50 ml, 0.0025 gmol of sodium tungstate, 0.005 gmol of PTC (TBAB) loading, speed of agitation = 1000 rpm). The rate of reaction was observed to increase with increase in reaction temperature up to 60^0C. The calculated activation energy from the Arrhenius plot for the temperature range of 40^0C-60^0C is 10 kcal/gmol (Figure 2), which indicates that the reaction is kinetically controlled.

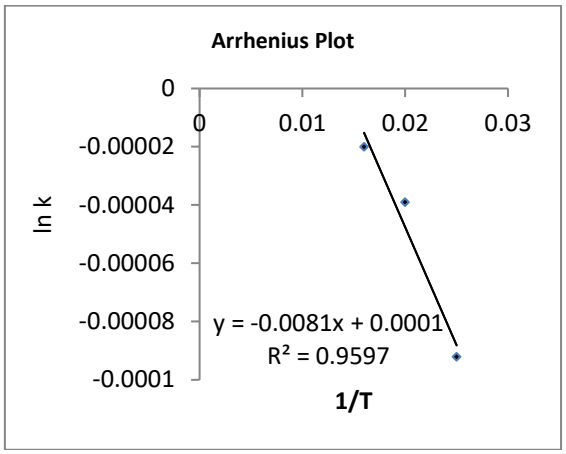


Figure 2: Arrhenius Plot

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 0.0022 gmol/cm^3 to 0.0044 gmol/cm^3 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, 0.0025 gmol of sodium tungstate, 0.005 gmol of PTC (TBAB) loading, speed of agitation = 1000 rpm, temperature = 333K). A plot of $-\ln(1-X_A)$ versus time (Figure 3) at 333 K was found to be linear which shows that the reaction is first order with respect to the concentration of cyclohexanol and this suggests that mass transfer effects are negligible which is in agreement with the high value of activation energy obtained.

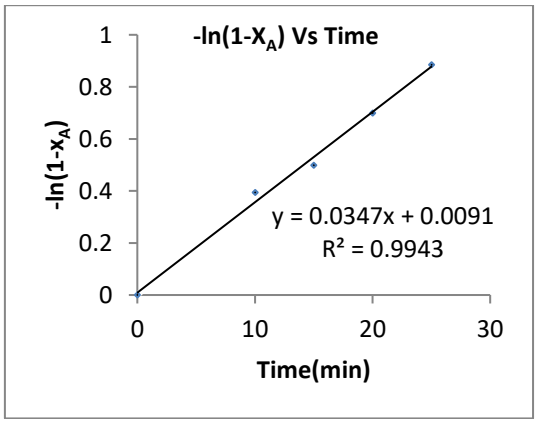


Figure 3: Plot of -ln(1-X_A) v/s Time

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 0.0044 gmol/cm^3 to 0.0088 gmol/cm^3 under otherwise similar conditions (namely 0.44gmol cyclohexanol, organic phase made up to 100 ml with ethyl acetate as solvent, aqueous phase (30% w/v H_2O_2) volume = 50 ml, 5 mol % of PTC (TBAB) loading, speed of agitation = 1000 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 4 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 of hydrogen peroxide.

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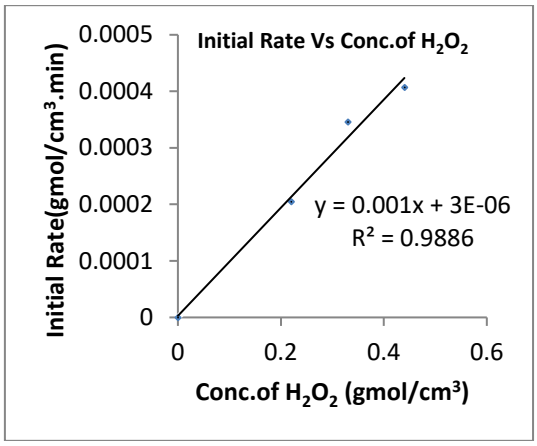


Figure 4: Initial Rate of Reaction v/s Concentration of H_2O_2

Effect of Phase Transfer Catalyst Loading:

The effect of phase transfer catalyst loading on the oxidation of cyclohexanol was studied by varying the phase transfer catalyst (tetrabutyl ammonium bromide, TBAB) loading from 0.005 gmol to 0.015 gmol (based on cyclohexanol) under otherwise similar conditions (namely, 0.44 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, 0.0025 gmol of sodium tungstate, speed of agitation = 1000 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 5 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.

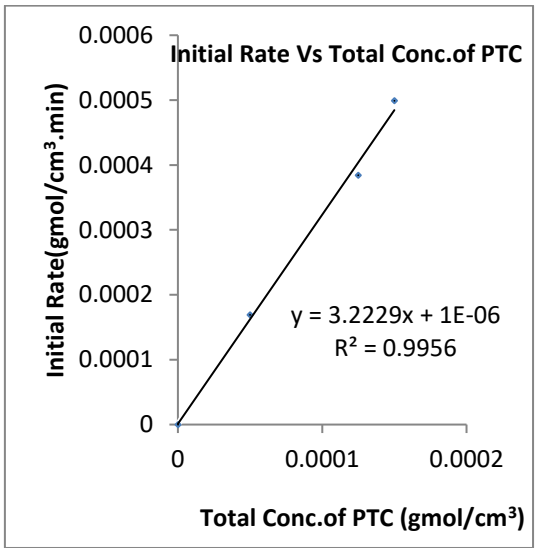


Figure 5: Initial Rate of Reaction v/s Total Concentration of PTC

Effect of Co-catalyst Loading:

The effect of co- catalyst loading on the oxidation of cyclohexanol was studied by varying the co-catalyst (sodium tungstate, $Na_2WO_4.2H_2O$) loading from 0.0025 gmol to 0.0075 gmol (based on cyclohexanol) under otherwise similar conditions (namely, 0.44 gmol 1-cyclohexanol, organic phase made up to 100 ml with ethyl acetate as solvent, aqueous phase (30% w/v H_2O_2) volume = 50 ml, 0.005 gmol of phase transfer catalyst, speed of agitation = 1000 rpm, temperature = 333K). A plot of initial rate of reaction versus concentration of the co-catalyst 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 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.

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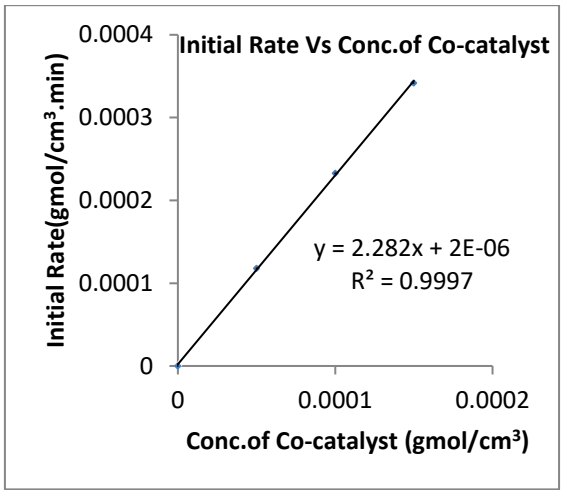


Figure 6: Initial Rate of Reaction v/s Concentration of Co-catalyst

CONCLUSION

The oxidation of cyclohexanol to cyclohexanone was successfully carried out with hydrogen peroxide as an oxidizing agent under liquid-liquid phase transfer catalysis with tetra butyl ammonium bromide as the phase transfer catalyst and sodium tungstate as the co-catalyst. It was observed that the rate of reaction increases with temperature, concentration of cyclohexanol, concentration of hydrogen peroxide, concentration of phase transfer catalyst and concentration of co-catalyst. The oxidation reaction was found to be kinetically controlled under the experimental conditions used. A kinetic model was developed to explain the experimental results obtained.

Conflict of Interest

The authors declare no conflict of interest.

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