Selective production of benzaldehyde by permanganate oxidation of benzyl alcohol using 18-crown-6 as phase transfer catalyst

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ABSTRACT

The oxidation of benzyl alcohol to benzaldehyde with potassium permanganate (KMnO$_4$) was studied in a batch reactor using 18-crown-6 (crown ether) as phase transfer catalyst in a solid–liquid system. Benzene was used as the solvent and KMnO$_4$ was taken as the solid reactant. KMnO$_4$ is not soluble in benzene in normal condition but the addition of 18-crown-6 forms a complex with KMnO$_4$ and makes it soluble in benzene. The oxidation reaction was studied at different degrees of agitation, temperature, catalyst concentration and mole ratio of benzyl alcohol to KMnO$_4$. The reaction usually occurs in two steps where the first step is the oxidation of benzyl alcohol to benzaldehyde and the second step is the formation of benzoic acid from benzaldehyde. In the chosen reaction condition benzaldehyde was obtained as the only product for all the cases. However, at higher temperature and substantial amount of catalyst concentration benzoic acid was obtained along with benzaldehyde. The initial rate was found to increase with increase in concentration of catalyst (18-crown-6) and benzyl alcohol. A semi-empirical model for the reaction was depicted to illustrate the proposed mechanism. The activation energy and frequency factor of the reaction were found to be 9.149 kJ/mol and 1.85 × 10^6 respectively.

1. Introduction

Permanganate, a well-known oxidant, is generally used in aqueous solutions and this restricts its application in oxidation of many organic compounds as most of them are not soluble in water. The cavity in the crown ether can accommodate an alkali metal ion through ion–dipole interaction to form an alkali cation–crown ether complex with a counter anion [1,2]. By this way they increase the salt solubility and increase anion reactivity in organic solvents. Under the phase transfer catalysed condition, permanganate is soluble in benzene and the resulting solution can be used as oxidizing agent [3–6]. Mechanism and kinetics of oxidation of different organic compounds with potassium permanganate with or without catalysts have been discussed and reported by many researchers [7–12]. Use of a phase transfer catalyst in two phase system of benzene and potassium permanganate made the two phases miscible to each other forming 'purple benzene' as reported by Herriott et al. [13] and proposed to be a method of choice for oxidation of organic compounds. Use of tetrabutyl ammonium bromide as phase transfer catalyst in permanganate oxidation of many aromatic aldehydes and alcohols into their corresponding acids and

ketones with a high yield have been reported by Sala and Sargent [14]. Crown ether as a phase transfer catalyst in permanganate oxidation of different arenes, ketones and alcohols has also been found in the literature [5]. The rates of oxidation of substituted catechol with permanganate in both liquid–liquid and solid–liquid modes have been investigated with different polarity solvents and reported to increase with addition of crown ether [15]. The metal fluoride complex with crown ether has been reported to show good oxidation ability to a variety of organic substrates [16].In this work, the oxidation of benzyl alcohol to benzaldehyde with potassium permanganate in presence of 18-crown-6 as phase transfer catalyst has been investigated.The ability of 18-crown-6 to dissolve permanganate in benzene is utilized in pursuing this reaction. The present work deals with the study of the effects of different process parameters on this reaction which has not been reported earlier. The kinetics of the reaction has also been studied.

2. Experimental

2.1. Materials

Potassium permanganate, benzene, benzyl alcohol, benzaldehyde and benzoic acid were procured from M/s Marck Specialities Pvt. Ltd., Mumbai, India. 18-crown-6 was obtained as gift sample from Dishman Chemicals and Fertilisers, Mumbai, India.

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Nomenclature

C_{QKMnO_4} Concentration of QKMnO$_4$ complex, kmol l^{-1}
C_Q Concentration of crown ether, kmol l^{-1}
C_{KMnO_4} Concentration of solid KMnO$_4$
C_{QK^+} Concentration of QK$^+$ complex, kmol l^{-1}
$C_{MnO_4^-}$ Concentration of MnO$_4^-$ ion, kmol l^{-1}
C_A Concentration of benzyl alcohol, kmol l^{-1}
C_I Concentration of intermediate, kmol l^{-1}
K_A Constant defined in Eq. (2), dimensionless
K_D Dissociation constant defined in Eq. (3), dimensionless
k_2, k_{-2} Rate constants of forward and reverse reaction respectively defined in step (C) of the mechanism, l kmol^{-1} min^{-1}
k_3 Rate constant of the reaction defined in step (D) of the mechanism, l kmol^{-1} min^{-1}
k Rate constant in Eq. (10), l kmol^{-1} min^{-1}
k' Rate constant in Eq. (12), l$^{1/2}$ kmol$^{-1/2}$ min^{-1}
r_2 Rate of the reaction of step (C), kmol l^{-1} min^{-1}
r_3 Rate of the reaction of step (D), kmol l^{-1} min^{-1}
r_P Initial rate of benzaldehyde formation, kmol l^{-1} min^{-1}
r_{P_1}, r_{P_2} Rate of benzaldehyde formation, kmol l^{-1} min^{-1}

2.2. Experimental setup

A three necked cylindrical glass vessel of 250 cm^3 capacity, i.d. 7 cm fitted with a condenser and a four bladed turbine glass stirrer was used for the reaction. The temperature was controlled at $\pm 1\,^\circ$C by a thermocouple using an electrically heated waterbath.

2.3. Procedure

In a typical run, 0.7 ml (0.003 mol) of catalyst was added to a solution of 7.6 gm KMnO$_4$ (0.048 mol) in 100 ml benzene (1.1264 mol) and stirred until clear purple solution appeared. 5 ml of benzyl alcohol (0.048 mol) was added to the reactor and taken as the starting point of the reaction. Benzyl alcohol was chosen as the limiting reactant in the entire experiment. The samples collected at the time interval of 5 min up to 125 min, were analyzed in HPLC using a 25-cm reverse phase C-18 column with mobile phase as acetonitrile and water in the ratio of 7:3 with a flow rate of 1 ml/min. The wavelength of UV detector was kept at 254 nm.

3. Reaction mechanism and kinetic model

The reaction between benzyl alcohol and potassium permanganate in benzene using 18-crown-6 as phase transfer catalyst follows a solid–liquid phase transfer mechanism. Crown ether captures potassium ion into its cage structure and forms a complex ion in benzene which subsequently dissociates into two conjugate ions QK$^+$ and MnO$_4^-$. The reaction mechanism proposed is shown in Fig. 1. The MnO$_4^-$ ion then attacks benzyl alcohol and a transition complex (I) is formed which consequently gives benzaldehyde and manganic acid. As one crown ether molecule can take up only one potassium ion into its cage hole, the concentration of crown ether may be assumed to be the same as that of QKMnO$_4$ ion. If the ion pair QKMnO$_4$ completely dissociates then its concentration will be the same as QK$^+$ as well as MnO$_4^-$ ion which actually acts as the oxidizing agent for the reaction. There is another probability where QKMnO$_4$ does not dissociate completely. In that case the concentration of QKMnO$_4$ will not be equal to the concentrations of QK$^+$

and MnO$_4^-$ ions where the concentrations of the latter two will be equal. So two models for the reaction can be derived considering two conditions (a) complete dissociation of QKMnO$_4$ and (b) partial dissociation of QKMnO$_4$. Potassium permanganate used was very fine powder, so we can neglect the mass transfer resistance between permanganate and crown ether. In the present study, amount of potassium permanganate was always higher than that of catalyst.

The overall reaction can be written as

$$PhCH_2OH + KMnO_4 \xrightarrow{Crown\,Ether} PhCHO + H_2MnO_4 \qquad (1)$$

Assuming all individual steps are elementary and step (D) as rate determining step, the rate equation is obtained as follows:

$$Step\,A: \quad K_A = \frac{C_{QKMnO_4}}{C_Q C_{KMnO_4}} \qquad (2)$$

where KMnO$_4$ is in solid form, so, C_{KMnO_4} does not exist.

$$Step\,B: \quad K_D = \frac{C_{QK^+} C_{MnO_4^-}}{C_{QKMnO_4}} = \frac{C_{MnO_4^-}^2}{C_{QKMnO_4}} \qquad (3)$$

$$r_2 = k_2 C_A C_{MnO_4^-} - k_{-2} C_I \qquad (4)$$

$$r_3 = k_3 C_I \qquad (5)$$

$$\frac{dC_I}{dt} = k_2 C_A C_{MnO_4^-} - k_{-2} C_I - k_3 C_I = 0 \qquad (6)$$

$$C_I = \frac{k_2}{k_{-2} + k_3} C_A C_{MnO_4^-} \qquad (7)$$

By substituting C_I in Eq. (5) we get,

$$r_P = r_3 = \frac{k_3 k_2}{k_{-2} + k_3} C_A C_{MnO_4^-} = k C_A C_{MnO_4^-} \qquad (8)$$

where

$$k = \frac{k_3 k_2}{k_{-2} + k_4} \qquad (9)$$

Case 1: if we assume the dissociation of QKMnO$_4$ is complete in benzene, we may write $C_Q \cong C_{MnO_4^-} \cong C_{QKMnO_4}$, then Eq. (8) may be written as

$$r_{P_1} = k C_A C_Q \qquad (10)$$

Case 2: if QKMnO$_4$ partially dissociates, then from Eq. (3) we may write

$$C_{MnO_4^-} = \sqrt{K_D} C_{QKMnO_4}^{1/2} \qquad (11)$$

The rate equation is obtained as

$$r_{P_2} = k' C_A C_Q^{1/2} \qquad (12)$$

where

$$k' = \frac{k_3 k_2 \sqrt{K_D}}{k_{-2} + k_4}$$

The experimental data were fitted in the above rate Eqs. (10) and (12) to find out the proper rate model.

4. Results and discussion

The reaction between benzyl alcohol and KMnO$_4$ is assumed to be a bimolecular reaction where in each case benzyl alcohol was taken in a lesser amount than KMnO$_4$ to make benzyl alcohol as the limiting reaction and subsequently all conversions are calculated based on benzyl alcohol.

$$Q \ + \ KMnO_4 \ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \ \left[QKMnO_4 \right]_b \ \text{------------(A)}$$

$$\left[QKMnO_4 \right]_b \ \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} \ QK^+ \ + \ MnO_4^- \ \text{------------(B)}$$
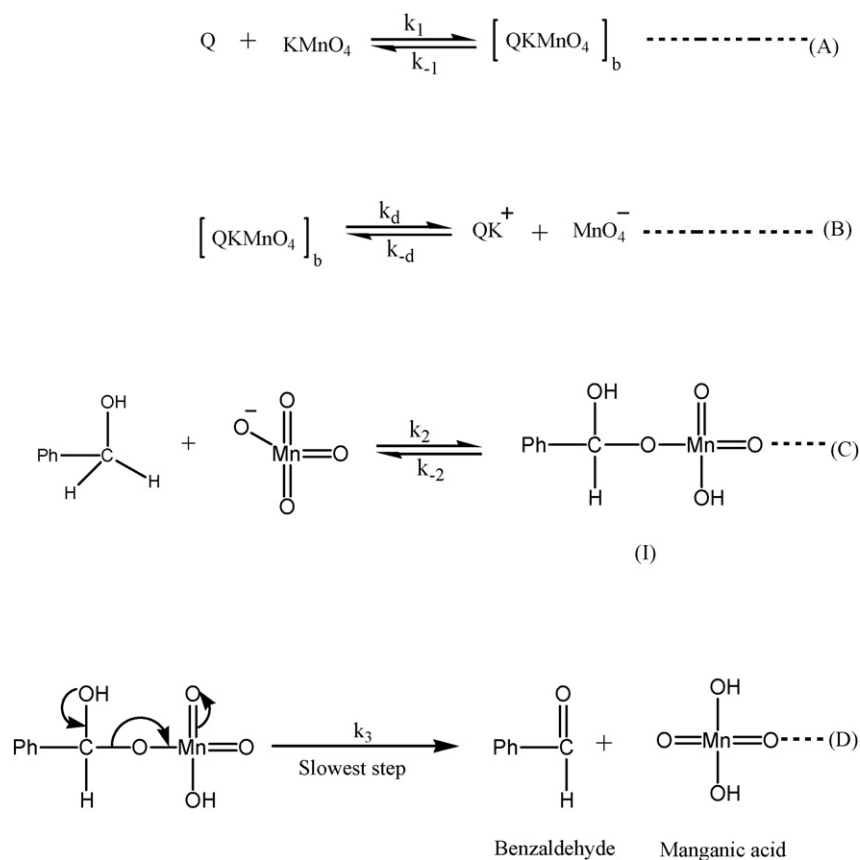

(I)

Benzaldehyde   Manganic acid

Fig. 1. Mechanism of the reaction.

4.1. Effect of speed of agitation

The effect of speed of agitation on the conversion of benzyl alcohol was studied at different speeds of agitation in the range of 600–1200 rpm. It is evident from Fig. 2 that the conversion of benzyl alcohol increases as the speed of agitation is increased till 1000 rpm and beyond that speed the increase is negligible. The conversion increases from 34% at 600 rpm to 43% at 1000 rpm. A few experiments were conducted without stirring and it was found that no conversion of benzyl al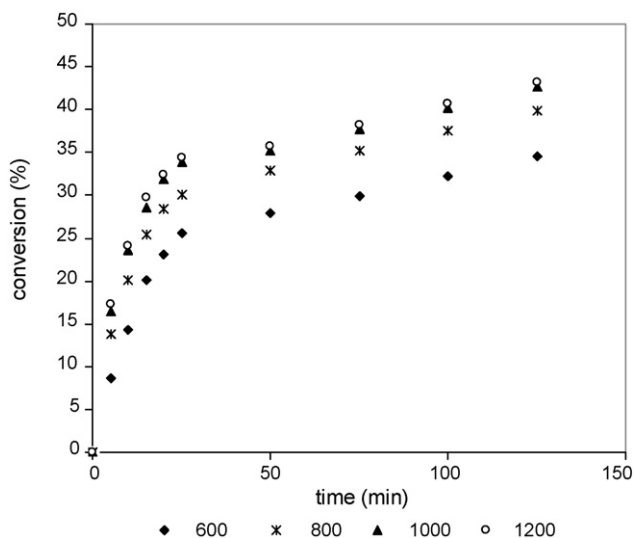cohol was obtained. As solid potassium permanganate is added in the crown ether and benzene mixture, the dissolution of $KMnO_4$ is influenced by the speed of agitation due to enhancement of mass transfer. So with the increase in the number of $QKMnO_4$ complex and subsequent ionization to QK^+ and MnO_4^-, the benzyl alcohol conversion increases. Fig. 2 establishes this phenomenon.

4.2. Effect of moles of benzyl alcohol

The change in mole of benzyl alcohol was investigated using 1.6, 2.6 and 3.6 mol in 100 ml benzene. It was observed that the sole product was benzaldehyde. The conversion of benzyl alcohol to benzaldehyde is increased with the increase in moles or concentration of benzyl alcohol in benzene as expected which is shown in Fig. 3. The conversion at three different moles 1.6, 2.6 and 3.6 at 30 min time are found to be 3.4%, 4.1% and 5.1%. So, we may conclude that conversion of benzyl alcohol is varying almost linearly with its concentration.

The concentrations of benzyl alcohol with the progress of reaction were calculated and plotted against time in Fig. 4. The initial rates at three different concentrations of benzyl alcohol at $t = 0$ were determined from the slopes of the tangents of the plots of Fig. 4 and these initial rates are fitted against concentrations of benzyl alcohol (Fig. 5). As the correlation coefficient is close to unity, we may infer that the rate of reaction is first order with respect to benzyl alcohol concentration for constant temperature and C_Q.

4.3. Effect of catalyst concentration

The effect of catalyst concentration on the progress of oxidation of benzyl alcohol was studied at fixed concentrations of both the reactants. Fig. 6 shows how the conversion increases with time for
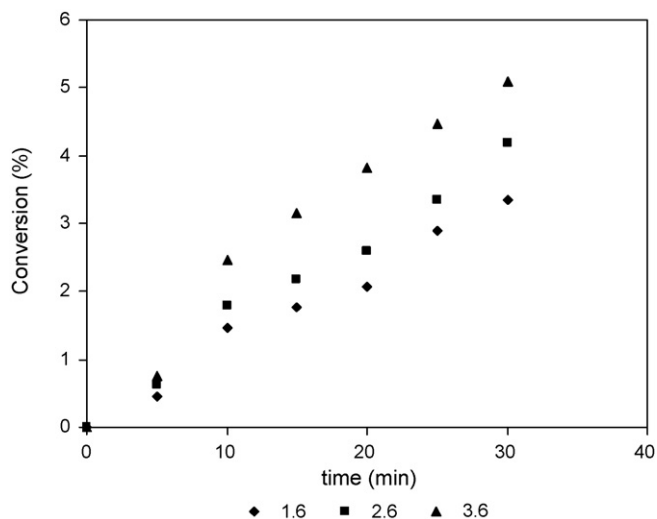

Fig. 2. Effect of speed of agitation on conversion of benzyl alcohol.
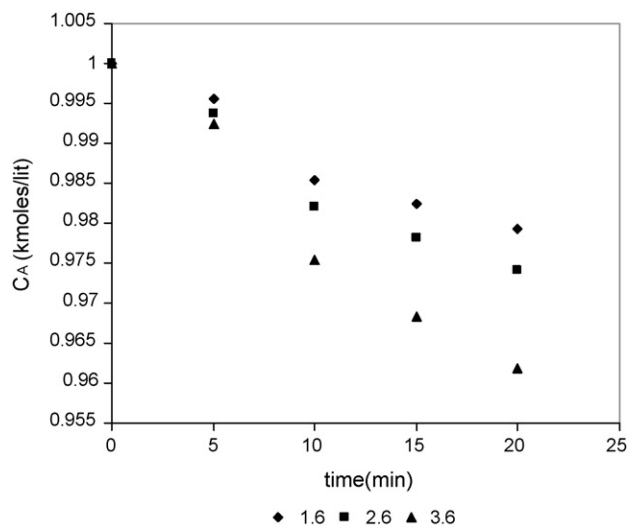
Fig. 3. Effect of increase in moles of benzyl alcohol on conversion.

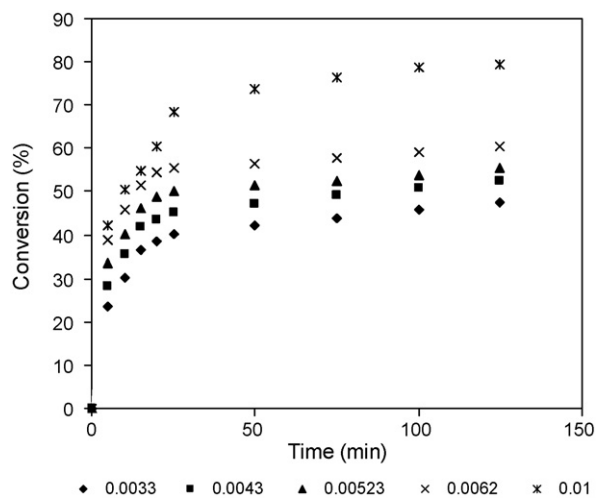**Fig. 6.** Effect of catalyst loading on conversion.

various crown ether concentrations. With the increase in catalyst concentration, the conversion was increased. This can be illustrated by the fact that more number of crown ether molecules produces more number of QKMnO$_4$ complex which results in the formation of more number of MnO$_4{}^-$ ion available for the oxidation reaction. The concentrations of benzyl alcohol (C_A) at different times were calculated from conversion data and were plotted against time which has been shown in Fig. 6.

According to our model (Eqs. (10) and (12)) derived for this reaction the initial rate obtained from the slope of the tangents at $t = 0$ from Fig. 7. The initial rates plotted against C_Q and $C_Q^{1/2}$ at different catalyst concentrations are shown in Figs. 8 and 9 respectively. The better correlation coefficient (0.9945) for Eq. (10) than that of Eq. (12) (0.9766) is obtained where rate is directly proportional to the catalyst concentration (C_Q). It can be interpreted from this result that QKMnO$_4$ is completely dissociating in the solution into QK$^+$ and MnO$_4{}^-$.

4.4. Effect of temperature

Effect of reaction temperature on the progress of oxidation of benzyl alcohol was studied in the temperature range 293–343 K. Conversion of benzyl alcohol was increased with increase in reaction temperature as shown in Fig. 10.
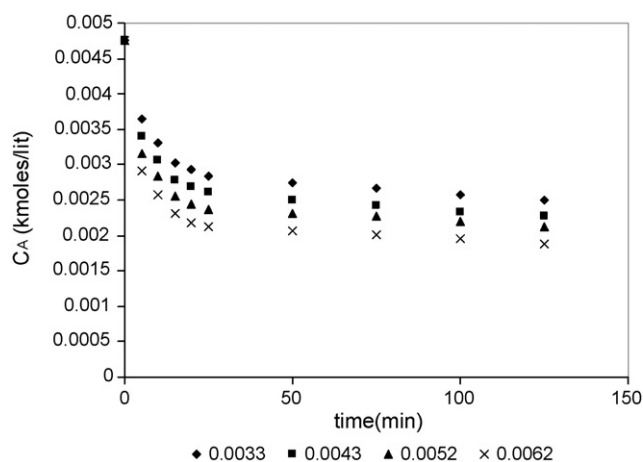

Fig. 4. Plot of change in concentration of benzyl alcohol with time.

Fig. 5. Plot of initial rate at different benzyl alcohol concentration (kmol l^{-1}).

Fig. 7. Plot of change in concentration of benzyl alcohol with time at different moles of crown ether.

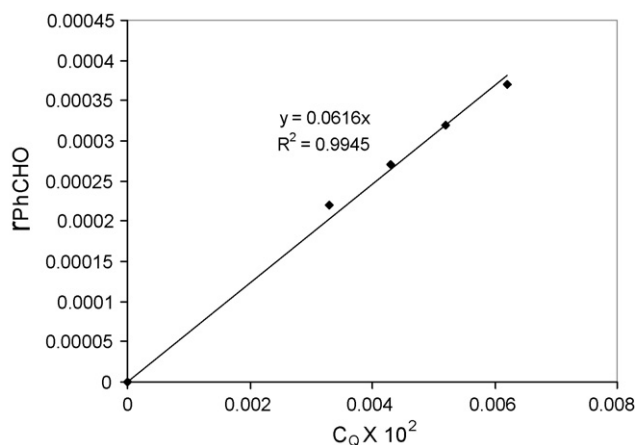**Fig. 8.** Fitting plot of initial rate at different crown ether concentration (mol l^{-1}) following Eq. (10).

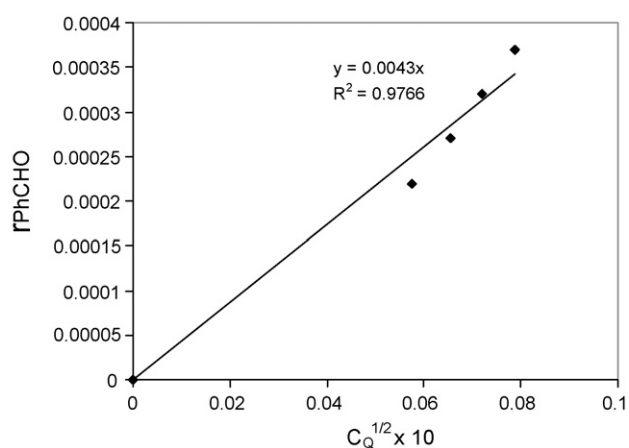**Fig. 11.** Arrhenius plot.

The activation energy was calculated from the slope of ln k_0 vs. $1/T$ plot (Fig. 11) as 9.149 kJ/mol and frequency factor as 1.85×10^6.

4.5. Formation of benzoic acid with change in reaction condition

The oxidation of benzyl alcohol follows series reaction where in the first step benzyl alcohol oxidizes to benzaldehyde and consequently in the next step benzaldehyde oxidizes to benzoic acid. In all the previous cases benzaldehyde was obtained as the sole product and no benzoic acid was detected. An interesting feature is observed when reaction condition is changed; benzaldehyde and benzoic acid both are formed as products. Figs. 12 and 13 depict the variation in conversion of benzyl alcohol to benzoic acid with time at two different temperatures and two different catalyst amounts. From Fig. 12 it is seen that the conversion of benzyl alcohol to benzoic acid at 120 min is about 10% at 303 K for 0.01 mol crown ether, but benzoic acid formation is negligible when 0.0033 mol catalyst is used at the similar reaction condition.

Fig. 13 shows the variation in conversion to benzoic acid when the reaction occurs at 343 K keeping all other reaction parameters same. At this higher temperature, using 0.0033 and 0.01 mol catalyst, conversion to benzoic acid was obtained in both the cases which are about 4% and 12% respectively at the same reaction condition. In the previous condition, benzaldehyde was selectively obtained without any formation of benzoic acid. As the severity of

Fig. 9. Fitting plot of initial rate vs. square root of different crown ether concentration (mol l^{-1}) following Eq. (12).

The rate constant (k_0) at different temperatures were calculated from initial rate data following the equation:
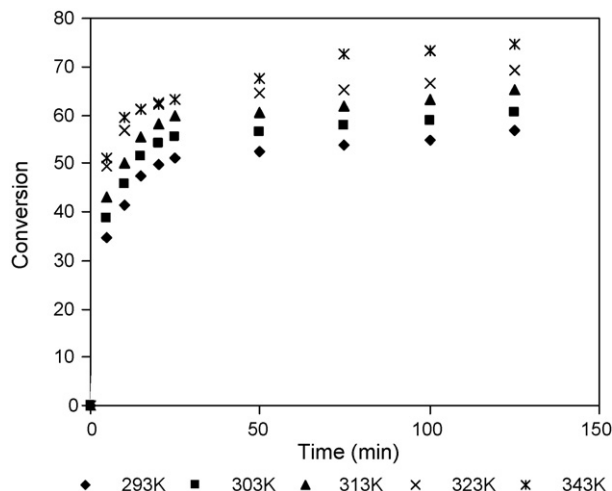
$$k_0 = \frac{r_P}{C_{A0}C_{Q0}}$$
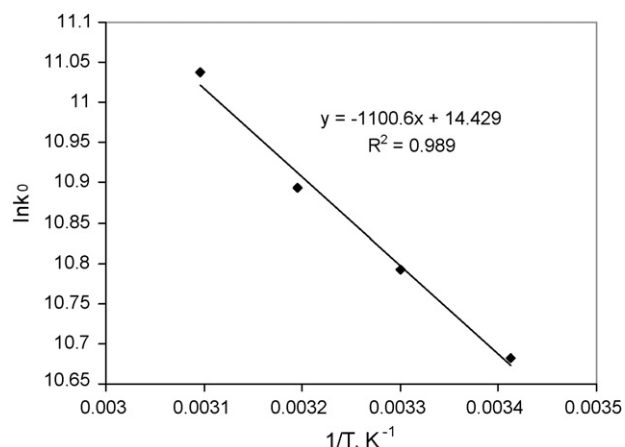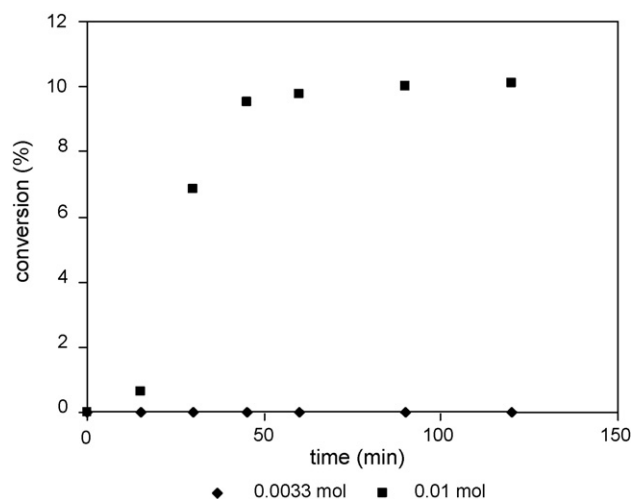

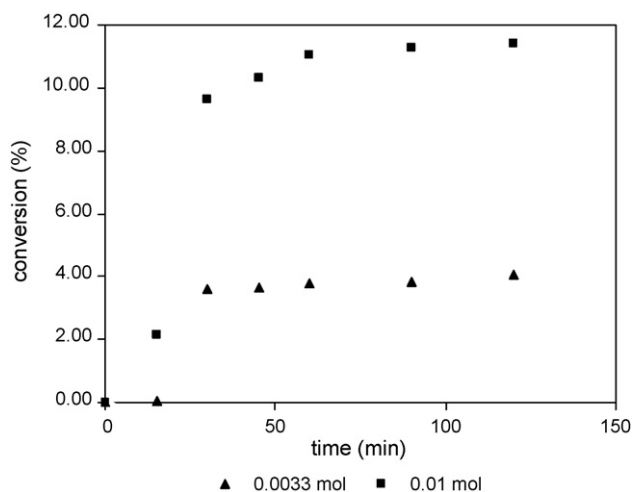**Fig. 10.** Effect of temperature on conversion.

Fig. 12. Variation in conversion to benzoic acid with variation in catalyst amount at 303 K.

Fig. 13. Variation in conversion to benzoic acid with variation in catalyst amount at 343 K.

the reaction increases i.e., higher temperature and higher amount of catalyst, the second step of the reaction occurs and some amount of benzaldehyde was oxidized to benzoic acid in this step. So it may be inferred that the second step of this series reaction may have higher activation energy than that of the first step.

5. Conclusions

The present work comprises the phase transfer catalysed oxidation of benzyl alcohol. The catalyst employed was 18-crown-6 and $KMnO_4$ was used as oxidant in solvent benzene. The catalyst helps to solubilise $KMnO_4$ in benzene phase. By proper selection of process variables it was possible to obtain benzaldehyde as the only product. However, both benzaldehyde and benzoic acid formation were observed by conducting reaction at higher temperature and higher catalyst amount. A homogeneous rate equation was developed and fitted successfully with the experimental data. The activation energy and frequency factor of benzaldehyde formation reaction step were found to be 9.149 kJ/mol and 1.85×10^6 respectively. In this work, the aim was to get benzaldehyde in high conversion and selectivity which has been attained successfully at the chosen reaction parameters.

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