

Oxidation of benzyl alcohol under a synergism of phase transfer catalysis and heteropolyacids

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Abstract

The use of heteropolyacids in conjunction with phase transfer catalysts in the oxidation of benzyl alcohol to benzaldehyde with hydrogen peroxide as the oxidising agent has been investigated. The effect of various parameters on the conversion of benzyl alcohol was studied including the effect of the nature of the heteropolyanion as well as the effect of the partial substitution of protons in the heteropolyacid. Surfactant-type phase transfer catalysts were found to display high catalytic activity with cetyltrimethylammonium bromide (CTMAB) being the most effective phase transfer catalyst among those examined. A suitable mechanism for this reaction has been proposed and a kinetic model has been developed in order to explain the observed experimental results. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Oxidation; Benzyl alcohol; Benzaldehyde; Phase transfer catalysis; Heteropolyacids; Synergism; Kinetic model

1. Introduction

Benzaldehyde is a very important raw material or intermediate which has widespread applications in the perfumery, pharmaceutical, dyestuff and agrochemical industries [1]. It is mainly produced as a co-product with benzoic acid by the oxidation of toluene. The oxidation of benzyl alcohol under controlled conditions can lead to benzaldehyde as the major product. Depending upon the reaction conditions and the type of oxidising agent used, different by-products are also formed, which are mainly benzoic acid and benzyl benzoate [2,3].

Hydrogen peroxide (H_2O_2) is a clean and environmentally friendly reagent which has widespread use

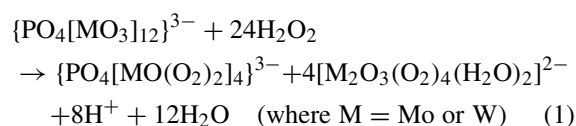
in the oxidation of organic compounds. However, its use is limited by the fact that most valuable organic substrates and aqueous H_2O_2 are mutually insoluble. This serious limitation has been circumvented with the aid of phase transfer catalysis (PTC), a well known technique in organic synthesis [4].

The use of co-catalysts with PTC has proven to be advantageous in intensifying the rates of oxidation reactions with H_2O_2 . The co-catalysts could be tungsten trioxide [5], sodium tungstate [6] or heteropolyacids such as dodeca-tungstophosphoric acid and dodeca-molybdophosphoric acid [7].

The first mechanistic study of heteropolyacid catalysed oxidations with H_2O_2 in biphasic reaction media was carried out by Ishii et al. [8] who proposed a conceivable epoxidation path via a peroxy-type intermediate in the epoxidation of olefins with H_2O_2 catalysed by heteropolyacids combined with cetylpyridinium chloride (CPC).

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The study of the interaction of excess hydrogen peroxide with heteropolytungstates or molybdates [9] has clearly shown that their catalytic properties for oxidation are mainly related to the loss of their polyanionic structure, in particular when the heteropolyacids $H_3[PM_{12}O_{40}]$ ($M = Mo$ or W) are used. An overall reaction describing the degradation of the heteropolyacids with Keggin structure in the presence of excess hydrogen peroxide is proposed:



The biphasic epoxidation of 1-octene by H_2O_2 with CPC as the PTC was examined in the presence

of a variety of heteropolyacids and transition metal-substituted and silylated polyoxometalates (Ishii–Venturello epoxidation) [10]. The high catalytic activity exhibited by $[PW_{12}O_{40}]^{3-}$ and $[PW_{11}O_{39}]^{7-}$ could be explained by the fact that these polytungstophosphates are extremely labile and form the active oxidising species, viz. $[PO_4\{WO(O_2)_2\}_4]^{3-}$ most readily. A reaction mechanism and kinetic model has also been developed for the Ishii–Venturello epoxidation of olefinic compounds such as undecylenic acid and styrene [11,12].

Subsequent to the initial reports on Ishii–Venturello chemistry, Neumann and Khenkin [13] showed that transition metal catalysed oxidations carried out in liquid–liquid biphasic reaction media using hydrogen peroxide as oxygen donor and quaternary ammonium

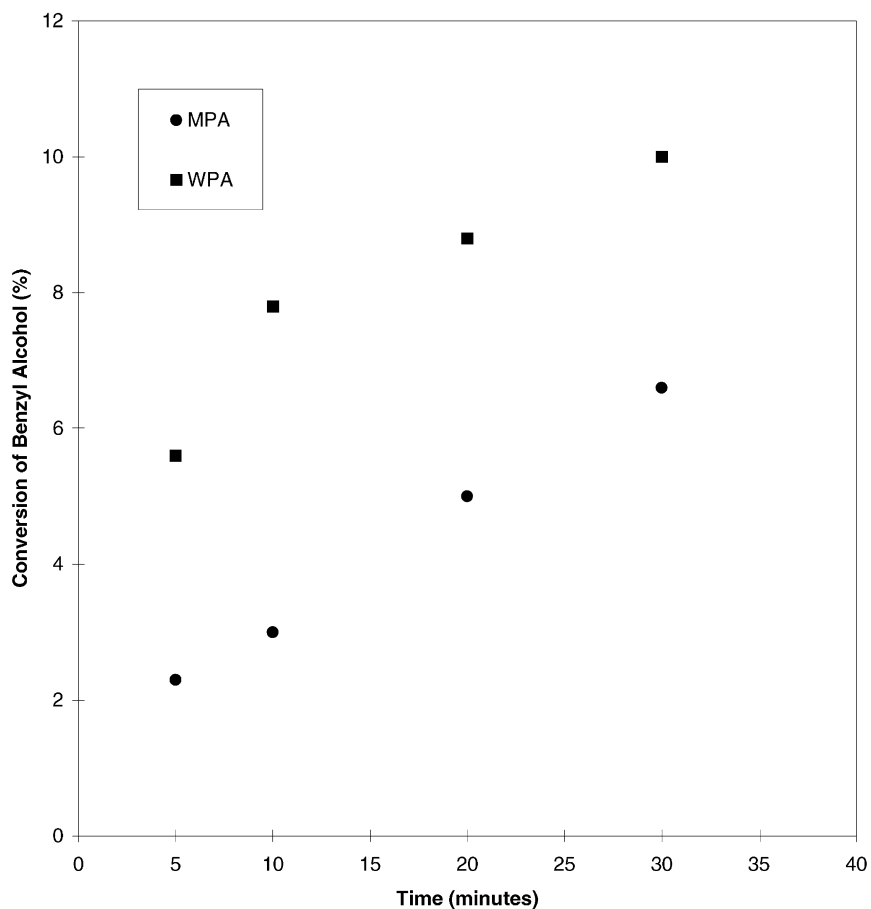


Fig. 1. Effect of the nature of the heteropolyanion.

cations were reactions in inverse emulsions and not typical phase transfer catalysed reactions. Surfactant-type phase transfer catalysts were found to be more active than the non-surfactant-type phase transfer catalysts.

Most of the available literature on the mechanism of reactions catalysed by heteropolyacids or polyoxometalates with hydrogen peroxide as the oxidising agent in biphasic reaction media deal with the epoxidation of olefins or olefinic compounds. The results obtained from these studies could be extended to other systems such as the oxidation of benzyl alcohol since many aspects of the reaction mechanism would remain essentially the same under typical Ishii–Venturello chemistry conditions.

2. Experimental procedure

Hydrogen peroxide (30%, w/v AR) was obtained from M/s S.D. Fine-Chem Ltd., Mumbai, India and its exact concentration was determined by iodometry [14]. All the other chemicals and catalysts used in this research work were obtained from firms of repute.

The reactions were studied in a mechanically agitated contactor of 200 cm³ total capacity equipped with a six-blade pitched turbine impeller, four equispaced baffles and a reflux condenser. All of the required amount of the 30% (w/v) hydrogen peroxide solution was put into a 100 ml beaker containing the appropriate amount of the heteropolyacid (HPA) along with 1 ml of water. After 5 min of stirring

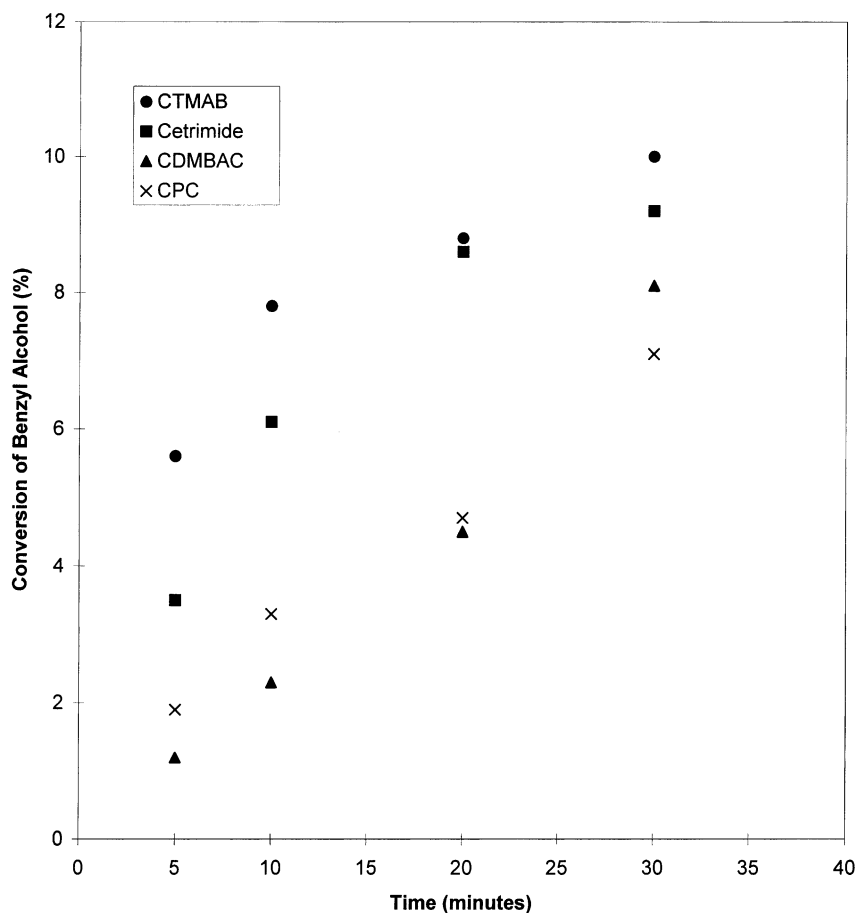


Fig. 2. Effect of different surfactant-type phase transfer catalysts.

(necessary for the heteropolyacid to dissolve and react completely), the aqueous phase was transferred to the reactor, where the reaction would be carried out in which the organic phase (containing the required amount of benzyl alcohol and the phase transfer catalyst in carbon tetrachloride (CCl_4) as the solvent and the total volume of the organic phase V_o , made up to 100 ml) was already present. The reactor was then placed in an oil bath maintained at the desired temperature and the reaction mixture was stirred at the required speed of agitation. The reaction was carried out for the desired time period and samples of the organic phase were withdrawn at definite intervals and filtered before being taken for analysis by gas chromatography.

The organic phase samples were analysed by a Chemito 8510 gas–liquid chromatograph with a flame

ionisation detector (FID). A stainless steel column packed with 10% SE-30 supported on Chromosorb W(HP) was used for the analysis. Synthetic mixtures were prepared and used for calibration and quantification.

3. Development of theoretical model

Based on the previous studies, a reaction mechanism has been proposed for the oxidation of benzyl alcohol to benzaldehyde with hydrogen peroxide under a synergism of phase transfer catalysis and heteropolyacids. The mechanism 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.

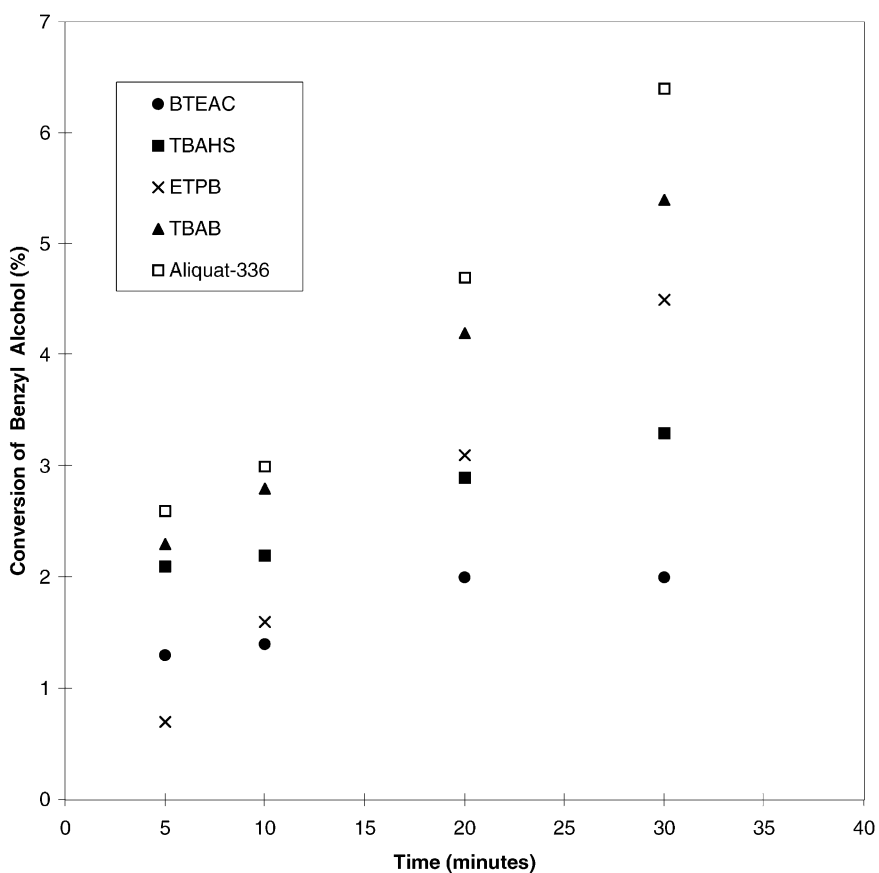
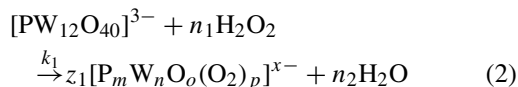


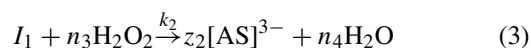
Fig. 3. Effect of different non-surfactant-type phase transfer catalysts.

1. Reaction between the heteropolyacid, e.g. dodeca-tungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) and hydrogen peroxide (H_2O_2) in the aqueous phase to generate the intermediate peroxy species I_1 , namely $[\text{P}_m\text{W}_n\text{O}_o(\text{O}_2)_p]^{x-}$:



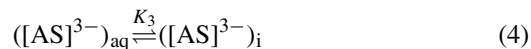
where z_1 , n_1 and n_2 are stoichiometric coefficients.

2. Reaction of the intermediate peroxy species I_1 , with H_2O_2 subsequently in the aqueous phase to produce the active oxidising species $[\text{AS}]^{3-}$, namely $\{\text{PO}_4[\text{W}(\text{O})(\text{O}_2)_2]_4\}^{3-}$:



where z_2 , n_3 and n_4 are stoichiometric coefficients.

3. Transfer of the active oxidising species $[\text{AS}]^{3-}$, from the aqueous phase to the interfacial region:



where the subscripts 'aq' and 'i' represent the aqueous phase and the interfacial region, respectively.

4. If it is assumed that simple ion exchange across the interface between the organic phase and the interfacial region takes place, then the mechanism of transfer of the active oxidising species by the accessible quaternary ammonium salt to

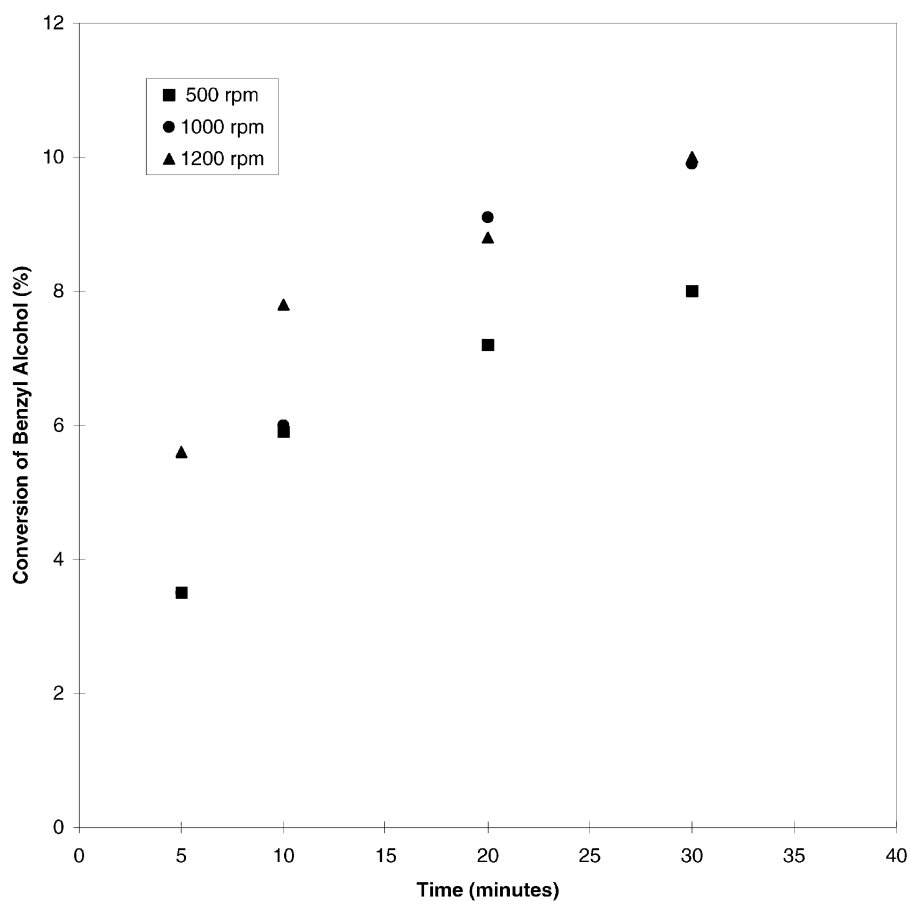
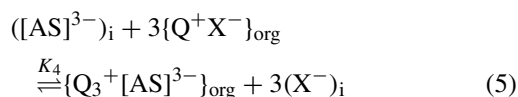


Fig. 4. Effect of speed of agitation.

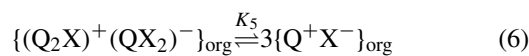
the organic phase may be written as



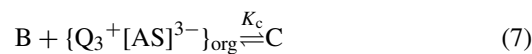
A certain amount of the halide ion (X^-) formed in this step is transferred to the aqueous phase, where it could react with the free hydrogen ions (H^+) generated by the dissociation of the heteropolyacid (viz. $\text{H}_3\text{PW}_{12}\text{O}_{40}$) to produce HX .

It is also possible that in non-polar solvents, e.g. carbon tetrachloride (CCl_4) the accessible phase transfer catalyst undergoes aggregation. It could be assumed that a higher aggregate is the dominant species present, although a small equilibrium concentration of the monomeric ion pair is the reactive species [4]. The following

equilibrium would exist in the organic phase:



5. Reaction of $\{\text{Q}_3^+[\text{AS}]^{3-}\}$ present in the organic phase with one molecule of benzyl alcohol ($\text{C}_6\text{H}_5\text{CH}_2\text{OH}$) B to form an intermediate C:



6. Reaction of the intermediate C with another molecule of benzyl alcohol in the organic phase to give benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$), water (H_2O) and the subsequent peroxy species $[\text{SPS}]^{3-}$:

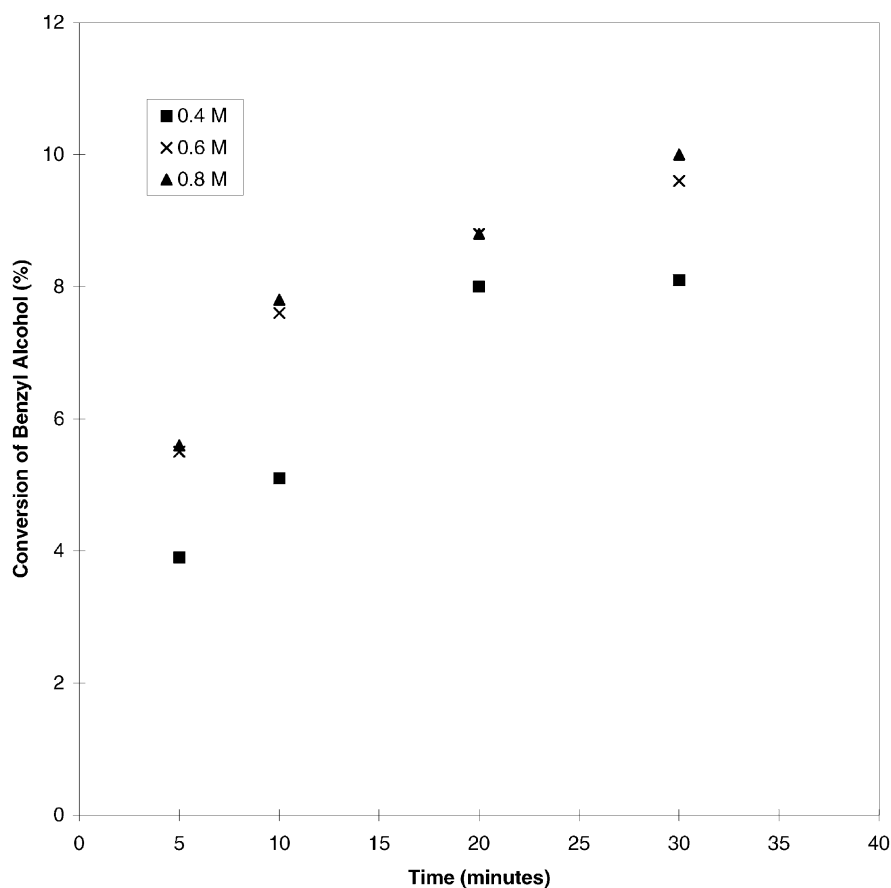
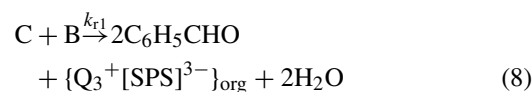
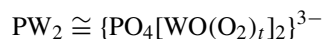
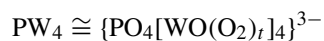
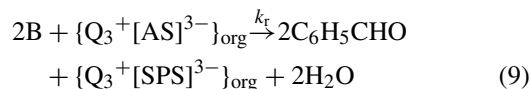


Fig. 5. Effect of concentration of benzyl alcohol $[\text{B}]_o$.

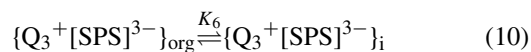
The subsequent peroxy species may be inferred to have the following formulae [11]:



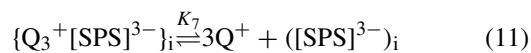
The overall oxidation reaction occurring in the organic phase is a combination of the above two steps and may be represented as follows:



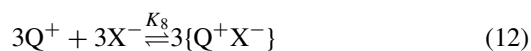
7. Transfer of the ion pair $\{Q_3^+[SPS]^{3-}\}$ from the organic phase to the interfacial region:



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



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



10. Transfer of water (H_2O) formed during the reaction from the organic phase to the interfacial region and then from the interfacial region to the aqueous phase:

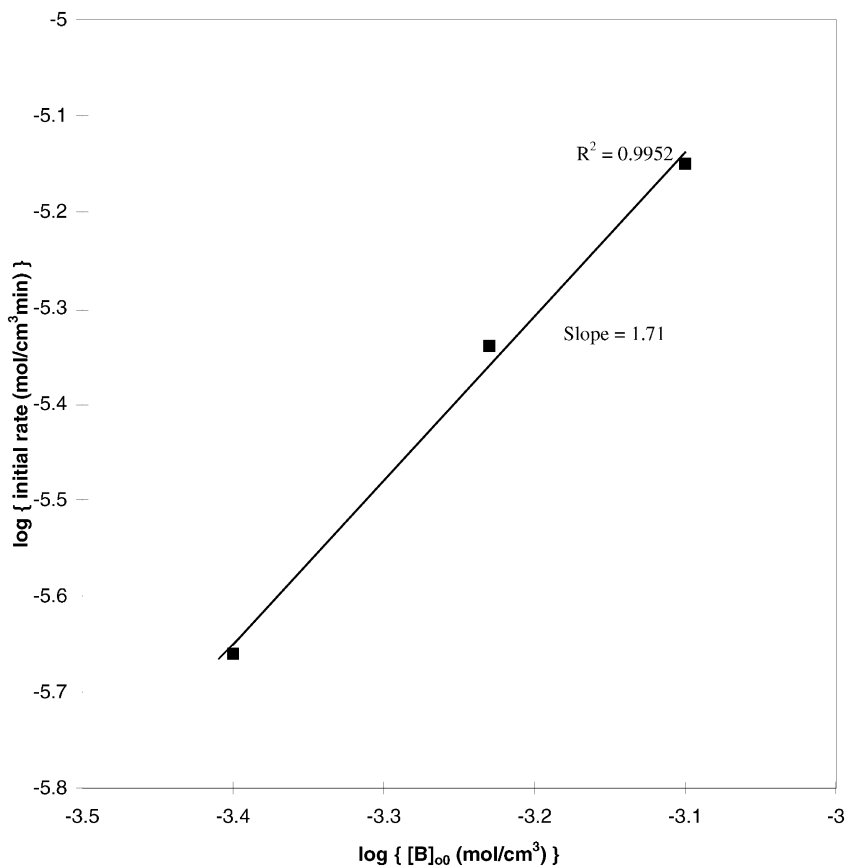
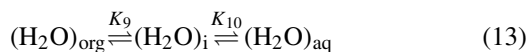
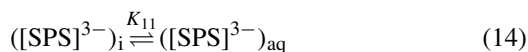


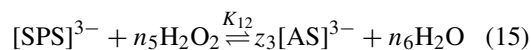
Fig. 6. Plot of log(initial rate) vs. log([B]₀₀).



11. Transfer of the subsequent peroxy species (SPS) from the interfacial region to the aqueous phase:



12. Reaction of the subsequent peroxy species (SPS) with H_2O_2 in the aqueous phase to regenerate the active oxidising species $[\text{AS}]^{3-}$:



where z_3 , n_5 and n_6 are stoichiometric coefficients.

In the above equations, k_1 , k_2 , k_{r1} 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} , K_{11} and K_{12} the equilibrium constants. Since the rates of steps 1, 2, 3, 4, 7, 8, 9, 10, 11 and 12 are assumed to be much greater than the rates of steps 5 and 6, these steps may be neglected while developing a suitable mathematical model. The relevant steps to be considered are steps 5 and 6.

If step 5 is assumed to be an equilibrium step and step 6 is assumed to be the rate controlling step, then the expression for the concentration of the intermediate C in the organic phase is:

$$[\text{C}]_{\text{o}} = K_c [\text{B}]_{\text{o}} [\text{Q}_a^+ \text{AS}^{3-}]_{\text{o}} \quad (16)$$

where the concentrations of the various species are shown in square brackets and the subscript 'o' indicates that the concentrations are in the organic phase. If it is assumed that the active oxidising species

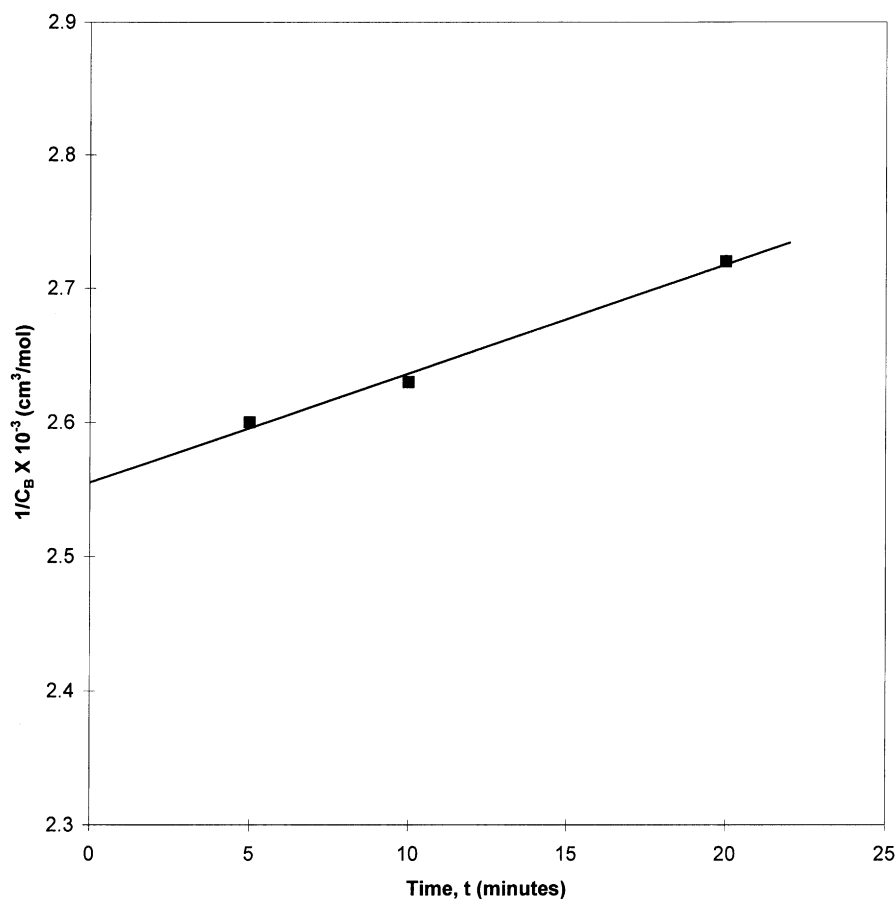


Fig. 7. Plot of $1/C_B$ vs. time.

$[AS]^{3-}$ 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

$$Q_o = [Q^+X^-]_o + [Q_3^+AS^{3-}]_o \quad (17)$$

If it is assumed that a higher aggregate of the accessible quaternary ammonium salt is the dominant species present in the organic phase, although a small equilibrium concentration of the monomeric ion pair is the reactive species, then Eq. (17) can be written as

$$Q_o = [(Q_2X)^+(QX_2)^-]_o + [Q_3^+AS^{3-}]_o \quad (18)$$

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 $\{(Q_2X)^+(QX_2)^-\}$ in constant proportion. This implies that:

$$\frac{[Q_3^+AS^{3-}]_o}{[(Q_2X)^+(QX_2)^-]_o} = \text{constant} = \phi \quad (19)$$

Eq. (19) can be substituted in Eq. (18) to give the expression:

$$[Q_3^+AS^{3-}]_o = \frac{\phi Q_o}{(1 + \phi)} \quad (20)$$

The rate of oxidation of benzyl alcohol to benzaldehyde in the organic phase is given by the expression:

$$r_B = \text{rate of oxidation} = k_{r1}[C]_o[B]_o \quad (21)$$

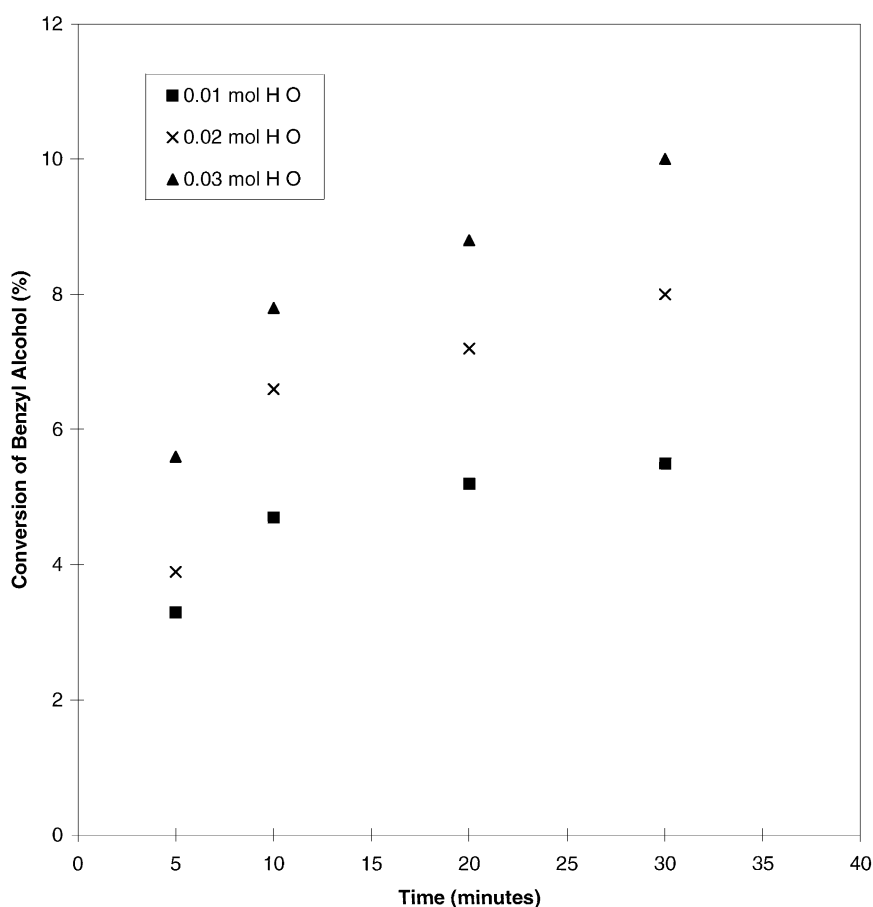


Fig. 8. Effect of amount of the oxidising agent.

Eqs. (16) and (20) can be used to obtain the following expression:

$$r_B = \frac{k_r \phi Q_o [B]_o^2}{(1+\phi)} \quad (22)$$

where $k_r = K_c k_{r1} =$ overall rate constant.

The above equation suggests the following:

1. the reaction is first-order with respect to the total concentration of the phase transfer catalyst in the organic phase, and
2. the reaction is second-order with respect to the concentration of benzyl alcohol in the organic phase.

Let $k_r \phi Q_o / (1 + \phi) = k_{ap2} =$ apparent rate constant and $[B]_o = C_B$, then Eq. (22) can be written as

$$r_B = -\frac{dC_B}{dt} = k_{ap2} C_B^2 \quad (23)$$

The above equation on integration gives:

$$\frac{1}{C_B} - \frac{1}{C_{B_0}} = k_{ap2} t \quad (24)$$

where C_{B_0} is the initial concentration of benzyl alcohol in the organic phase.

A plot of $1/C_B$ versus t should be linear. The value of the apparent rate constant k_{ap2} is obtained from the slope of the plot of $1/C_B$ versus t .

4. Results and discussion

The validity of the proposed theoretical model was tested against the experimental data obtained during the study of the effect of various reaction parameters. Preliminary experiments showed that there was no significant reaction in the absence of a phase transfer catalyst and the heteropolyacid, viz. dodeca-tungstophosphoric acid (WPA).

4.1. Effect of the nature of the heteropolyanion

The effect of the nature of the heteropolyanion was studied by using various heteropolyacids, viz. dodeca-tungstophosphoric acid (WPA), dodeca-molybdophosphoric acid (MPA) and dodeca-tungstosilicic acid (SWA). It was observed that WPA was found to be

very active in the oxidation of benzyl alcohol to benzaldehyde with hydrogen peroxide as the oxidising agent under biphasic conditions. MPA was also found to be catalytically active for the biphasic oxidation of benzyl alcohol, albeit at a lower level of reactivity than its tungsten analogue (Fig. 1). SWA did not exhibit any significant activity in this reaction. The lack of reactivity of SWA may reflect either the known lower rate of degradation of this complex by aqueous peroxide and the lower liability in general relative to WPA or the related point that the silicon analogue of $\{PO_4[WO(O_2)_2]_4\}^{3-}$ does not form in appreciable concentration under Ishii–Venturello conditions. In the absence of a heteropolyacid, the reaction did not proceed to any significant extent. Therefore, all further experiments were conducted with WPA as the heteropolyacid in the oxidation of benzyl alcohol with hydrogen peroxide under biphasic conditions.

4.2. Effect of different phase transfer catalysts

Various phase transfer catalysts were examined to evaluate their performance in this oxidation reaction. The catalysts studied were cetyltrimethylammonium bromide (CTMAB), Cetrimide (chiefly consisting of tetradecyltrimethylammonium bromide), cetyldimethylbenzylammonium chloride (CDMBAC), cetylpyridinium chloride (CPC), Aliquat-336 (tricaprylylmethylammonium chloride), tetrabutylammonium bromide (TBAB), ethyltriphenylphosphonium bromide (ETPB), tetrabutylammonium hydrogen sulphate (TBAHS) and benzyltriethylammonium chloride (BTEAC). It was observed that in general the surfactant-type phase transfer catalysts having a hydrophobic tail and a hydrophilic head viz. CTMAB, Cetrimide, CDMBAC and CPC were found to be more active than the non-surfactant-type phase transfer catalysts, viz. Aliquat-336, TBAB, ETPB, TBAHS and BTEAC (Figs. 2 and 3). CTMAB was found to exhibit the highest catalytic activity. In the absence of a phase transfer catalyst, there was no significant reaction. Therefore, the study of the effect of all the other reaction parameters was carried out with CTMAB as the phase transfer catalyst and dodeca-tungstophosphoric acid (WPA) as the co-catalyst.

The q values (q is a quantitative parameter for characterising accessibility) as defined by Starks et al.

[4] for CTMAB and Cetrimide are 3.06 and 3.07, respectively, indicating that these quaternary ammonium salts are very accessible and better catalysts than Aliquat-336 ($q = 1.38$), TBAB ($q = 1$) and TBAHS ($q = 1$). CDMBAC was not found to be as effective a catalyst as CTMAB or Cetrimide. In CDMBAC, the quaternary ammonium cation is not as accessible as in CTMAB or Cetrimide since it is attached to only two short methyl groups and one bulky benzyl group. In the case of CTMAB and Cetrimide, the quaternary cation is highly accessible since it is attached to three short methyl groups. CPC was also not found to be as effective a catalyst as CTMAB or Cetrimide. In CPC the quaternary cation is part of the heterocyclic six-membered pyridine ring and the positive charge on the quaternary cation may not be able to interact as closely with the anion or the active oxidising species as in the case of CTMAB and Cetrimide.

The use of phosphonium salts as phase transfer catalysts in this reaction was examined by using ethyl-triphenylphosphonium bromide (ETPB) as the phase transfer catalyst. The activity of ETPB was found to be less compared to the more active quaternary ammonium or pyridinium salts such as CTMAB, Cetrimide, CDMBAC, CPC, Aliquat-336 and TBAB.

4.3. Effect of speed of agitation

The effect of speed of agitation was studied by using various speeds, viz. 500, 1000, 1200 and 1500 rpm. As the speed of agitation was increased from 500 to 1200 rpm it was observed that the conversion of benzyl alcohol increased (Fig. 4). There was no significant increase in the conversion of benzyl alcohol when the speed of agitation was further increased from 1200 to 1500 rpm. In order to ensure that the reaction is

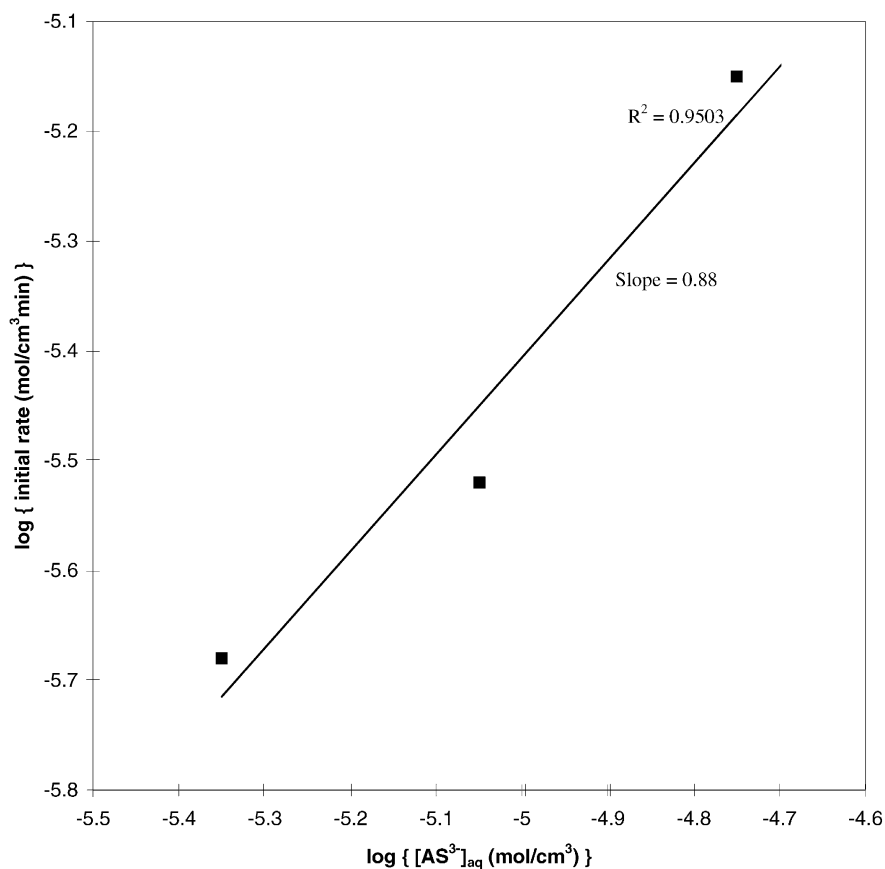


Fig. 9. Plot of $\log(\text{initial rate})$ vs. $\log([AS^{3-}]_{aq})$.

kinetically controlled all subsequent experiments were carried out at a speed of agitation of 1200 rpm.

4.4. Effect of concentration of benzyl alcohol

The effect of concentration of benzyl alcohol (BnOH) was studied by varying the concentration of BnOH from 0.4 to 0.8 M with CCl_4 as the solvent (Fig. 5). When the concentration of benzyl alcohol in the organic phase $[\text{B}]_0$, was increased from 0.4 to 0.6 M the conversion of benzyl alcohol was found to increase. Further increase in $[\text{B}]_0$ from 0.6 to 0.8 M resulted in no significant change in the conversion of benzyl alcohol.

The value of the slope of the plot of $\log(\text{initial rate of reaction})$ versus $\log(\text{initial concentration of benzyl$

alcohol), i.e. $\log([\text{B}]_{00})$ was found to be 1.71 (Fig. 6). This suggests that the reaction is second-order with respect to the concentration of benzyl alcohol in the organic phase. A plot of $1/C_B$ versus t was made for the lowest concentration of benzyl alcohol used in this study and was found to be linear (Fig. 7). The value of the apparent rate constant $k_{\text{ap}2}$ was calculated from the slope of the plot of $1/C_B$ versus t and found to be $8.14 \text{ cm}^3/\text{mol min}$.

4.5. Effect of amount of the oxidising agent

The effect of amount of the oxidising agent, viz. hydrogen peroxide (H_2O_2), was studied by using different number of moles of H_2O_2 , viz. 0.01, 0.02 and 0.03 mol. When the number of moles of H_2O_2 was

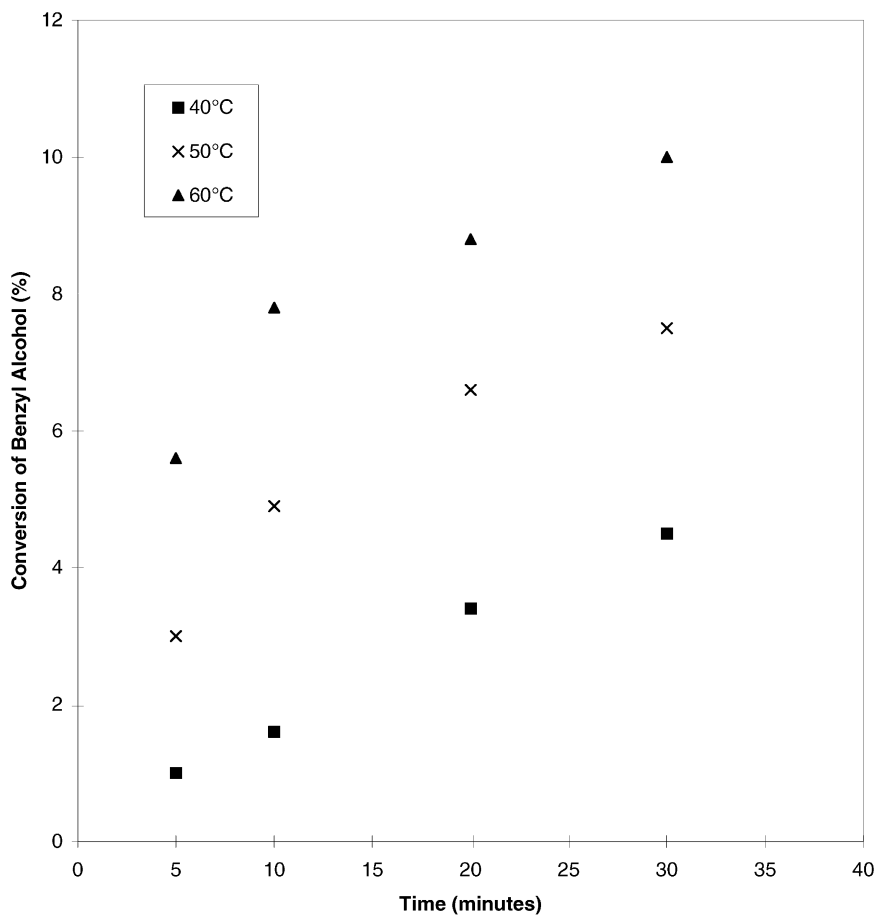


Fig. 10. Effect of temperature.

increased from 0.01 to 0.03 mol, the conversion of benzyl alcohol was found to increase (Fig. 8). Hydrogen peroxide was used as the limiting reactant under the given experimental conditions in order to minimise the formation of benzoic acid and benzyl benzoate.

4.6. Effect of concentration of the active peroxy species

The effect of the concentration of the active peroxy species was studied by using 0.02, 0.04 and 0.08 mmol of dodeca-tungstophosphoric acid (WPA) which were present in the aqueous phase ($V_{\text{aq}} \approx 4.5$ ml). The oxidation reaction was determined to be approximately first-order with respect to the concentration of the active oxidising species (or the active peroxy species, viz. $\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{3-}$ in the aqueous phase, $[\text{AS}^{3-}]_{\text{aq}}$, since the value of the slope of the plot

of $\log(\text{initial rate of reaction})$ versus $\log([\text{AS}^{3-}]_{\text{aq}})$ (Fig. 9) was found to be 0.88.

Since three equivalents of the phase transfer catalyst (viz. CTMAB) were used when the amount of WPA was varied, the reaction is also approximately first-order with respect to the total concentration of the phase transfer catalyst in the organic phase (Q_o). This indicates that aggregation of the accessible phase transfer catalyst, viz. CTMAB takes place in the organic phase [4].

4.7. Effect of temperature

The effect of temperature was studied by carrying out the reaction at various temperatures, viz. 40, 50 and 60°C. When the reaction temperature was increased from 40 to 60°C it was observed that the conversion of benzyl alcohol increased (Fig. 10). At higher

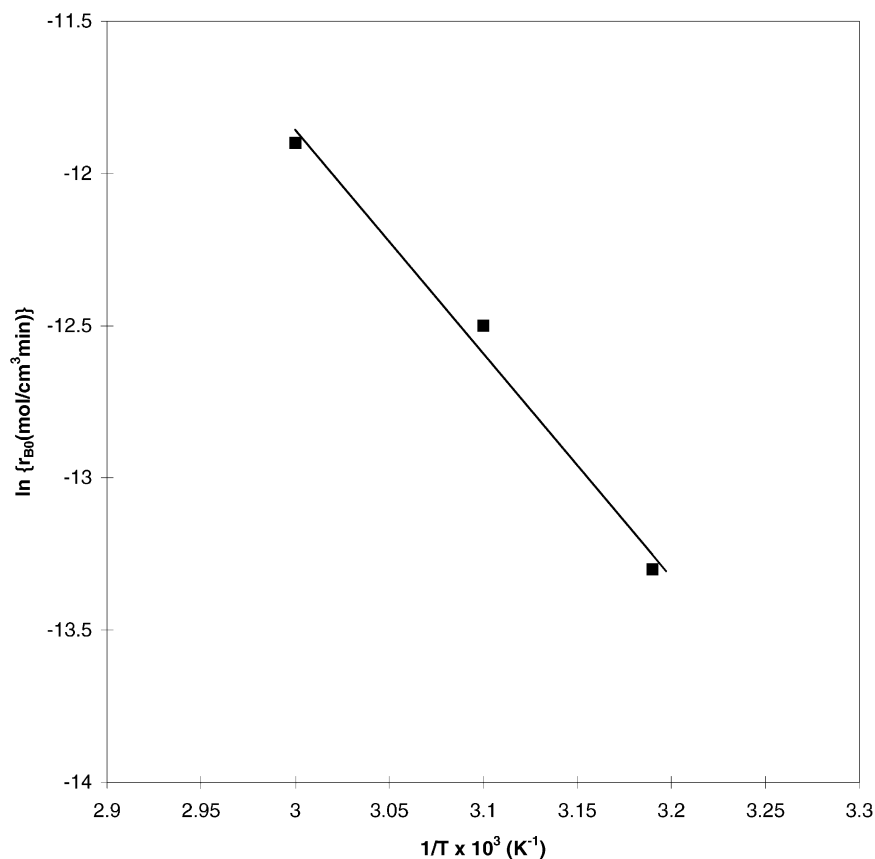


Fig. 11. Arrhenius plot.

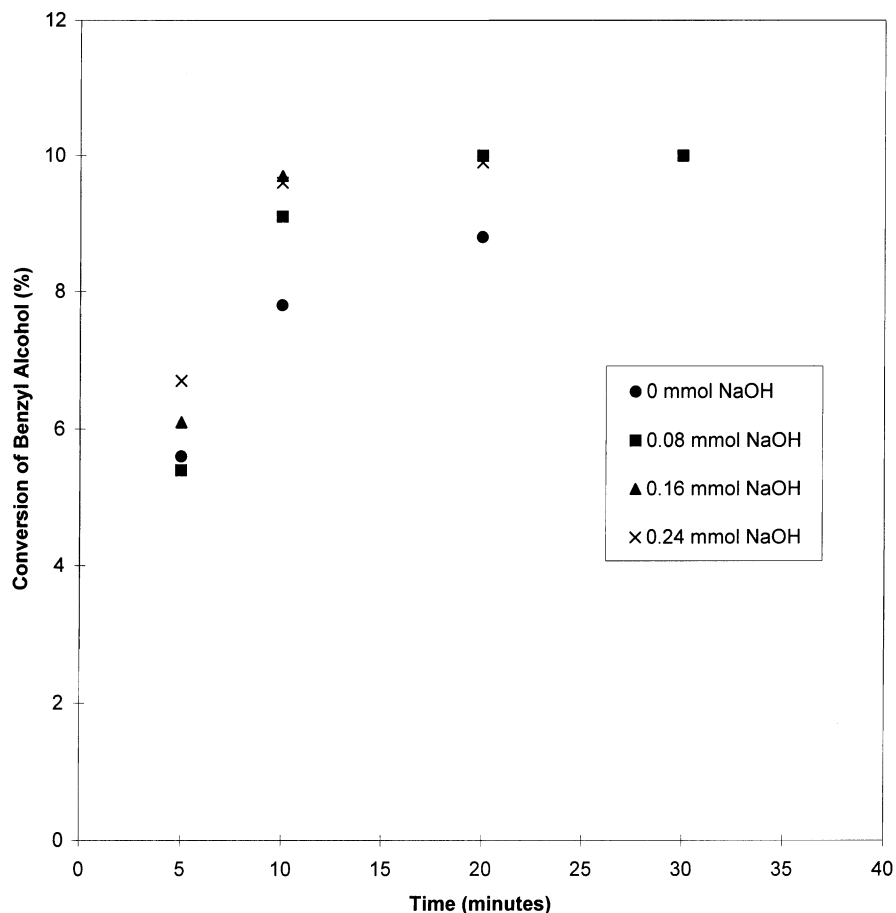


Fig. 12. Effect of partial substitution of protons in the heteropolyacid.

temperatures, decomposition of hydrogen peroxide may take place which is undesirable. The effect of temperature on the initial rate of reaction (r_{B_0}) was studied with the help of the Arrhenius plot as shown in Fig. 11. The value of the activation energy was calculated from the slope of the Arrhenius plot and found to be 14.1 kcal/mol. This value suggests that there is hardly any influence of mass transfer and that the reaction is kinetically controlled.

4.8. Effect of partial substitution of protons in the heteropolyacid

The effect of the partial substitution of protons in the heteropolyacid, viz. dodeca-tungstophosphoric

acid (WPA) was studied by adding 0.08, 0.16 and 0.24 mmol of sodium hydroxide (NaOH) to the aqueous solution of WPA before the addition of the aqueous hydrogen peroxide solution. The amounts of NaOH added correspond to 1, 2 and 3 equivalents of NaOH per equivalent (or mol) of WPA. It is observed that when 0.08 mmol of NaOH was added to the aqueous solution of WPA the catalytic activity was found to increase (Fig. 12). When the amount of NaOH added was increased to 0.16 and 0.24 mmol there was a further increase in the catalytic activity. Therefore, the catalytic activity is found to increase gradually with the drop in acidity when the protons in the heteropolyacid $H_3[PW_{12}O_{40}]$ are substituted by sodium (Na^+) ions.

5. Conclusions

A detailed investigation has been carried out on the use of heteropolyacids in conjunction with phase transfer catalysts in the oxidation of benzyl alcohol to benzaldehyde with hydrogen peroxide as the oxidising agent. Among the various heteropolyacids examined as co-catalysts, dodeca-tungstophosphoric acid (WPA) was found to significantly enhance the progress of the reaction. It was observed that in general the surfactant-type phase transfer catalysts were found to be more active than the non-surfactant-type phase transfer catalysts with cetyltrimethylammonium bromide (CTMAB) exhibiting the highest catalytic activity.

The reaction was found to be kinetically controlled at a speed of agitation greater than 1200 rpm. The value of the activation energy for the oxidation reaction was 14.1 kcal/mol which also suggests that the reaction is kinetically controlled. The oxidation reaction was found to be approximately first-order with respect to the concentration of the active oxidising species, viz. $\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{3-}$ in the aqueous phase. The experimental results indicate that aggregation of the accessible phase transfer catalyst, viz. CTMAB takes place in the organic phase and that the formation of reversed micelles is doubtful.

The catalytic activity is found to increase gradually with the drop in acidity when the protons in the heteropolyacid (WPA) are substituted by sodium ions. The reaction was found to be second-order with respect to the concentration of benzyl alcohol in the organic phase. A suitable mechanistic and kinetic model was developed to explain the observed experimental results.

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