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Kinetics of heterogeneous oxidation of benzyl alcohol with hydrogen peroxide

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Abstract

A clean catalytic process for the synthesis of benzaldehyde (BzH), with high selectivity, from benzyl alcohol (BzOH) by oxidation with hydrogen peroxide (H_2O_2), without any organic solvent in a batch reactor is studied.

Oxidation of BzOH to BzH was carried out at different speeds of agitation (800–1500 rpm), temperatures (343–363 K), catalyst loadings ($(3.4–5.9) \times 10^{-3}$ mol/L) and mole ratios of BzOH:H_2O_2 (1:1–1:2). Effect of various catalysts, e.g. tungstic acid, ammonium molybdate, and sodium tungstate and sodium molybdate on the oxidation of BzOH to BzH was studied. Ammonium molybdate was found to be the best catalyst for the oxidation of BzOH as compared to other catalysts. Increasing the speed of agitation beyond 1000 rpm has no significant effect on the rate of the oxidation of BzOH, indicating the absence of mass transfer resistance. Kinetics of the reaction have been established and values of activation energy have been reported.

Keywords: Oxidation; Benzyl alcohol; Benzaldehyde; Hydrogen peroxide; Tungstic acid; Ammonium molybdate

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1. Introduction

Aromatic aldehydes are important chemicals used in perfumes, soaps, foods and other products [1]. BzH is an important starting material for the manufacture of odorants and flavors, pharmaceutical intermediates.

It can be manufactured by oxidation of toluene, BzOH and dibenzyl ether using various oxidants and catalysts. Oxidation of alcohol is one of the most frequently used synthetic reactions in the laboratory and chemical manufacturing of aldehydes. Many researchers have reported synthesis of BzH by oxidation of BzOH using different combinations of H_2O_2 and catalysts [2–17]. Instead of inorganic oxidants, H_2O_2 is preferred as water is formed as a byproduct. Inorganic oxidants produce inorganic waste as a byproduct. Separation and disposal of this waste increase steps in the chemical process. Besides this, the waste deteriorates environment.

Brown patented a process for selective oxidation of alcohols to aldehydes or ketones. The process is particularly suitable for the oxidation of alcohols containing other oxidation sensitive groups such as carbon–carbon double bonds. Selective oxidation of alcoholic group takes place, in the presence of solvent containing no carboxyl groups and a tungsten containing catalyst comprising a heteropolyacid supported on an insoluble particulate support. Oxidation of BzOH with H_2O_2 in acetonitrile using tungstophosphoric acid/aluminium trioxide as a catalyst at 80 °C gave 43% conversion of benzyl alcohol with 74% selectivity of BzH [18]. Sato et al. reported halide-free oxidation of BzOH (925 mmol), by H_2O_2 (925 mmol) in the presence of methyl-tri-*n*-octyl ammonium hydrogen sulphate and tungstate (19 mmol) to get 86% BzH at 90 °C in 4 h [19]. Barak et al. reported direct oxidation of BzOH (91% conversion and 95% yield of BzH)with 30%, H_2O_2 (260 mmol) in the presence of didecyl dimethyl ammonium bromide as a phase transfer catalyst (1 mmol) and ruthenium trichloride trihydrate as a catalyst (0.077 mmol) [21]. Bortolini et al. obtained 96% yield of BzH in the oxidation of BzOH (0.02 mol) us-

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ing anionic molybdenum–peroxo complexes (0.15 mmol) in dichloroethane [20]. Venturello et al. used methyltrioctylammonium tetrakis (oxodiperoxotungsto) phosphate(III) (0.125 mmol) as a phase transfer catalyst in combination with H_2O_2 (25–37 mmol) for oxidation of BzOH (25 mmol) and obtained 77% yield of BzH together with 14% yield of benzoic acid [22]. Dengel et al. reported 40% yield of BzH in the oxidation of BzOH (18.5 mmol) by H_2O_2 (18.5 mmol) with tris-tetrakis-*n*-hexyl ammonium oxodiperoxotungsto phosphate(III) (0.03 mmol) at room temperature in benzene with a turnover of (1440) [23]. Bailey et al. studied the oxidation of BzOH (10 mmol) to BzH by H_2O_2 (46.25 mmol) with the bis-tetra-*n*-hexyl ammonium tetrakis peroxo tungsten trioxide(VI) (0.06 mmol) and di tetraphenylphoshino tetrakis peroxo tungsten trioxide (0.06 mmol). Ninety-six percent and 38% yield of BzH was obtained, respectively, with a turnover of 160 and 63 for these catalysts [24]. Griffith et al. have used the heteropolyperoxo complex $[(NMe_4)_2(PhPO_3)\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]$ as a catalyst (0.06 mmol) in the oxidation of BzOH (10 mmol) using H_2O_2 (44.1 mmol) and obtained BzH in 35% yield with a turnover of 71 [25]. Gresley et al. used tetra butyl ammonium diphenyl phosphineto bis-oxo-diperoxo tungsten(VI) as a catalyst (0.1 mmol) and $[N(C_6H_{13})_4]^+Cl^-$ (0.1 mmol) in the oxidation of BzOH (15 mmol) with H_2O_2 (46.25 mmol) and obtained 76% yield of BzH with a turnover of 114 [26]. Bhaumik and Kumar compared the triphasic conditions (solid and two immiscible liquid reactants) with biphasic ones (solid and immiscible liquids along with a co-solvent), stating that triphasic conditions significantly enhance the catalytic activity in the oxidation of BzOH by solid catalyst (TS-1, 20 wt.% with respect to the substrate), using H_2O_2. They observed that selectivity for BzH was 86% at 12.5% conversions in biphasic system with 14% selectivity for benzoic acid. In a triphasic system, conversions increased to 89.6% but selectivity of BzH decreased to 73.5%, and selectivity of benzoic acid increases to 25.6% [27]. From the literature cited, the phase transfer catalysis involves use of 1:1–1:0.07 (substrate:catalyst) catalyst for the oxidation of BzOH. Sato et al. had reported oxidation of BzOH to BzH using sodium tungstate and a phase transfer catalyst by H_2O_2 with 87% yield in 3 h [28].

In the available literature, kinetics of oxidation of BzOH with H_2O_2 in the presence of the catalyst are not available. So in the present work, kinetics of oxidation of BzOH is studied using H_2O_2 and tungstic acid/ammonium molybdate as a catalyst without any organic solvent.

$$C_6H_5CH_2OH + H_2O_2 \rightarrow C_6H_5CHO + 2H_2O \qquad (1)$$

2. Materials

BzOH, ammonium molybdate, sodium molybdate, sodium tungstate and H_2O_2 (30%, w/v) were procured from S.D. Fine Chemicals Ltd., Mumbai, India.

3. Experimental

All experiments were carried out in a borosilicate glass reactor of 60 mm i.d., 400 mL capacity provided with a six-blade turbine type impeller (20 mm diameter) and four baffles. Reaction temperature was maintained constant by immersing the reactor in a constant temperature oil bath. A predetermined quantity of BzOH (200 mmol), unless otherwise stated, was taken in the reactor, 200 mmol of H_2O_2 (unless stated otherwise) was added. All the reactants were brought to reaction temperature before adding to the reactor. The samples were withdrawn from the reaction mixture at predetermined time intervals. The separated organic phase was thoroughly washed with distilled water and analyzed by the gas chromatography. The aqueous phase was analyzed for H_2O_2 by iodimetric titration using potassium iodide and sodium thiosulphate.

4. Analysis

The analysis of the organic phase was carried out using the Chemito GC unit with 2 m long, 1/8 in., i.d. 10% OV17 column. Nitrogen was used as a carrier gas with FI detector. The GC program for the analysis of BzOH, BzH was as follows.

Injector temperature (°C)	350
Detector temperature (°C)	320
Initial temperature (°C) (hold = 6 min)	110
First ramp (°C/min)	25
Final temperature (°C) (hold = 3 min)	275
Carrier gas flow rates	
N_2 (mL/min)	12
H_2 (mL/min)	15
Air (mL/min)	15

5. Results and discussions

The kinetics of a liquid phase heterogeneous reaction can be studied, when the mass transfer resistance is eliminated. Therefore, the effect of speed of agitation on the progress of the reaction was studied first. The reaction progress was also investigated for different catalysts, mole ratio of reactants, catalyst loadings, and reaction temperature.

5.1. Speed of agitation

Experiments carried out at different speeds of agitation in the range of 800–1500 rpm, showed no effect on the rate of the oxidation of BzOH in this range indicating the absence of mass transfer resistance. All subsequent experiments were performed at 1500 rpm.

5.2. *Effect of different catalysts*

Oxodiperoxo and peroxo complexes of molybdenum and tungsten along with H_2O_2 are well known oxidants used for oxidation of organic compounds [29]. Metal-catalyzed epoxidations with H_2O_2 or alkyl hydroperoxides proceeds via formation of peroxometal species of early transition elements. Metals with low oxidation potentials and high Lewis acidity in their highest oxidation states are superior catalysts with the order of reactivity: Mo(VI) > W(VI) > V(V) > Ti(IV) [30]. In the presence of peroxomolybdenum complexes, no over oxidation to carboxylic acids occurs even if large excess of oxidants are used [31]. Ammonium molybdate and tungstic acid are among the most frequently used catalysts for oxidation of organic compounds with H_2O_2 [32]. Hence, in the present study these two together with sodium tungstate and sodium molybdate were selected as catalysts. Effect of these catalysts on the conversion of BzOH was investigated at 363 K. Ammonium molybdate gave highest conversion of BzOH compared to that with tungstic acid (Fig. 1) under otherwise identical conditions. In the presence of sodium tungstate and sodium molybdate practically no oxidation of BzOH was observed.

The highest conversion (77%) was obtained with ∼99% yield of BzH at a batch time of 300 min with ammonium molybdate (8.33×10^{-3} mol/L). Bortolini et al. observed that in the oxidation of BzOH with H_2O_2 catalyzed by tungsten(VI) complexes (1 mmol) in the presence of a phase transfer catalyst (aliquat 336, 2 mmol) at pH 1.4, gave 85% yield of BzH. They observed that excess H_2O_2 ranging from two-fold to six-fold leads to the formation of small amounts of benzoic acid instead of complete conversion of BzOH [33]. In the present case, H_2O_2 used was in the stoichiometric proportion and hence the formation of benzoic acid is negligible. Further, Conte et al. have reported that in the presence of peroxomolybdenum complexes, no over oxidation to carboxylic acid occurs even in the presence of excess of oxidants [31]. During these experiments, H_2O_2 in the reaction mixture was monitored. It was found that H_2O_2 was consumed very fast in the presence of sodium molybdate and sodium tungstate.

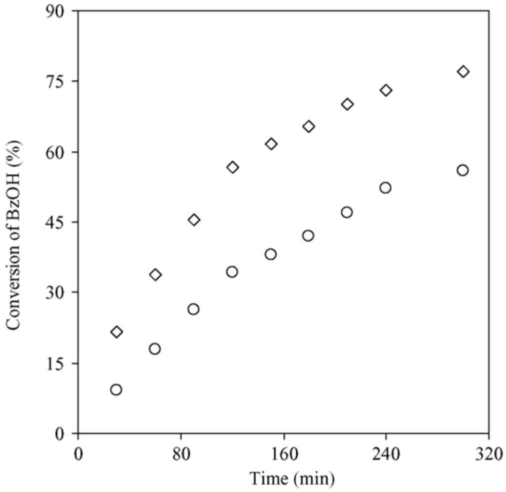

Fig. 1. Effect of different catalysts on the conversion of BzOH. BzOH: 0.2 mol; H_2O_2: 0.2 mol; total aqueous phase: 122.6 mL; temperature: 353 K; catalyst: 8.33×10^{-3} mol/L; (◊) ammonium molybdate; (◯) tungstic acid.

5.3. *Effect of mole ratio of reactants—(BzOH:H_2O_2)*

According to stoichiometry, one mole of H_2O_2 is required to give one mole of BzH from one mole of BzOH. Effect of 1:1, 1:2 mole ratio (BzOH:H_2O_2) was studied using ammonium molybdate as a catalyst. With 1:1 mole ratio (BzOH:H_2O_2), lower conversion of BzOH was observed (Fig. 2), as compare to the conversions obtained at 1:2 mole ratio.

A study on the material balance of H_2O_2 in the reaction mixture was carried out. It is consumed for oxidation of BzOH, lost due to decomposition and the balance remains unreacted in the reaction mixture. Unreacted H_2O_2 in the reaction mixture was determined iodometrically. H_2O_2 consumed for the formation of products was calculated, and then H_2O_2 decomposed was calculated by difference. At 343 K, consumption of H_2O_2 for oxidation of BzOH to BzH was less compared to that at higher temperature 353 K. Fig. 3 shows the ratio of H_2O_2 consumed for oxidation of BzOH to H_2O_2 self decomposed as a function of batch time. As the reaction temperature increases, the ratio increases. This indicates that H_2O_2 is more effectively consumed for the oxidation of BzOH at higher temperature.

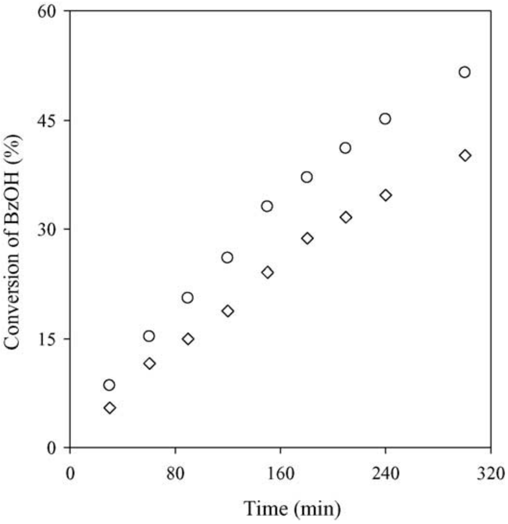

Fig. 2. Effect of H_2O_2 loading on the conversion of BzOH. BzOH: 0.2 mol; temperature: 353 K; (◯) 0.4 mol of H_2O_2—total aqueous phase: 145 mL; ammonium molybdate: 4.85×10^{-3} mol/L; (◊) 0.2 mol of H_2O_2—total aqueous phase: 122.5 mL; ammonium molybdate: 5.5×10^{-3} mol/L.

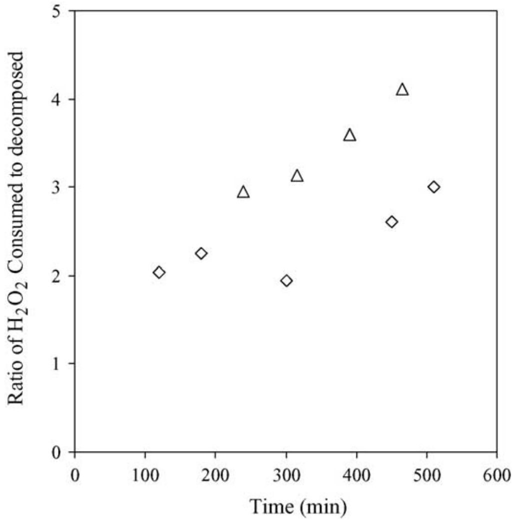

Fig. 3. Plot of ratio of H_2O_2 consumed for oxidation of BzOH to self-decomposed H_2O_2 vs. time (min). BzOH: 0.2 mol; H_2O_2: 0.2 mol; total aqueous phase: 122.6 mL; ammonium molybdenum: 9.76×10^{-3} mol/L; (△) 353 K; (◊) 343 K.

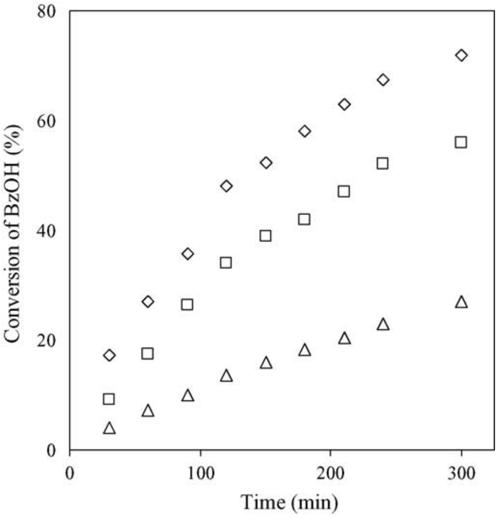

Fig. 5. Effect of tungstic acid loading on the conversion of BzOH. BzOH: 0.2 mol; H_2O_2: 0.2 mol; total aqueous phase: 122.6 mL; temperature: 363 K; (◊) 15.9×10^{-3} mol/L; (□) 8.3×10^{-3} mol/L; (△) 3.4×10^{-3} mol/L.

5.4. *Effect of catalyst loadings*

The effect of catalyst loading on the progress of oxidation of BzOH was studied separately with ammonium molybdate and tungstic acid as a catalyst (Figs. 4 and 5, respectively). The conversion increased from 52% to 77% with increase in the catalyst concentration from 3.4×10^{-3} to 8.3×10^{-3} mol/L for ammonium molybdate, while in the case of tungstic acid, it was 27–56% at the identical conditions. With further increase in tungstic acid concentration, (15.9×10^{-3} mol/L), 72% conversion of BzOH was obtained. This can be explained as the oxidation reaction proceeds via formation of a peroxo complex by a reaction between the catalyst and H_2O_2. This peroxo compound reacts with BzOH and eventually gives the product (Fig. 6). Thus, the higher catalyst concentration would mean higher concentration of the peroxo complex and hence faster consumption of BzOH.

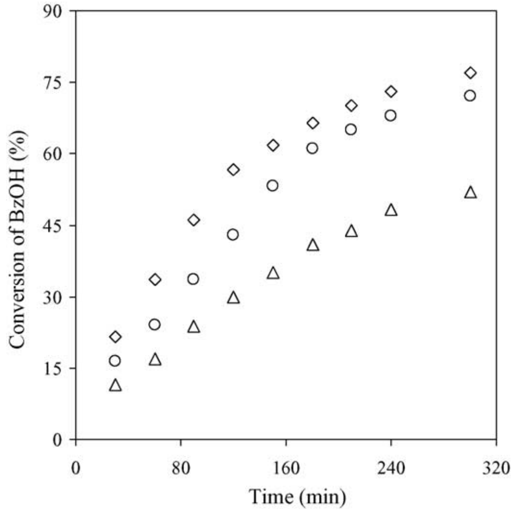

Fig. 4. Effect of ammonium molybdate loading on the conversion of BzOH. BzOH: 0.2 mol; H_2O_2: 0.2 mol; total aqueous phase: 122.6 mL; temperature: 363 K; (◊) 8.3×10^{-3}mol/L; (○) 5.5×10^{-3} mol/L; (△) 3.4×10^{-3} mol/L.

5.5. *Effect of temperature on the progress of the reaction*

Effect of reaction temperature on the progress of oxidation of BzOH was studied in the temperature range (343–363 K) at the mole ratio 2:2 (BzOH:H_2O_2). Conversion of BzOH increased from 22.5% to 75% in 300 min with increase in temperature from 343 to 363 K for ammonium molybdate (5.5×10^{-3} mol/L), and 14–55% for tungstic acid (8.3×10^{-3} mol/L), respectively. Conversion of BzOH increased with increase in the reaction temperature for both ammonium molybdate and tungstic acid as catalysts (Figs. 7 and 8).

6. Kinetics and mechanism

Zbigniew has reported the mechanism and kinetics of epoxidation of allyl alcohol by H_2O_2 with tungstic acid as a catalyst. A peroxo complex (intermediate) formed from the tungstic acid and H_2O_2 acts as an oxidizing agent [34]. Venturello and Ricci have proposed that the oxidative cleavage of 1,2-diols to carboxylic acids by H_2O_2 in the presence of catalytic amounts of tungstate and phosphate (or arsenate) ions proceeds via formation of peroxo intermediate [35]. Jacobson et al. have proposed a similar mechanism for the oxidation of monohydric alcohols catalyzed by oxodiperoxo (picolinate) tungstate(VI) [36].

Thus, in the present case, a mechanism involving formation of peroxo complex formed by the reaction between H_2O_2

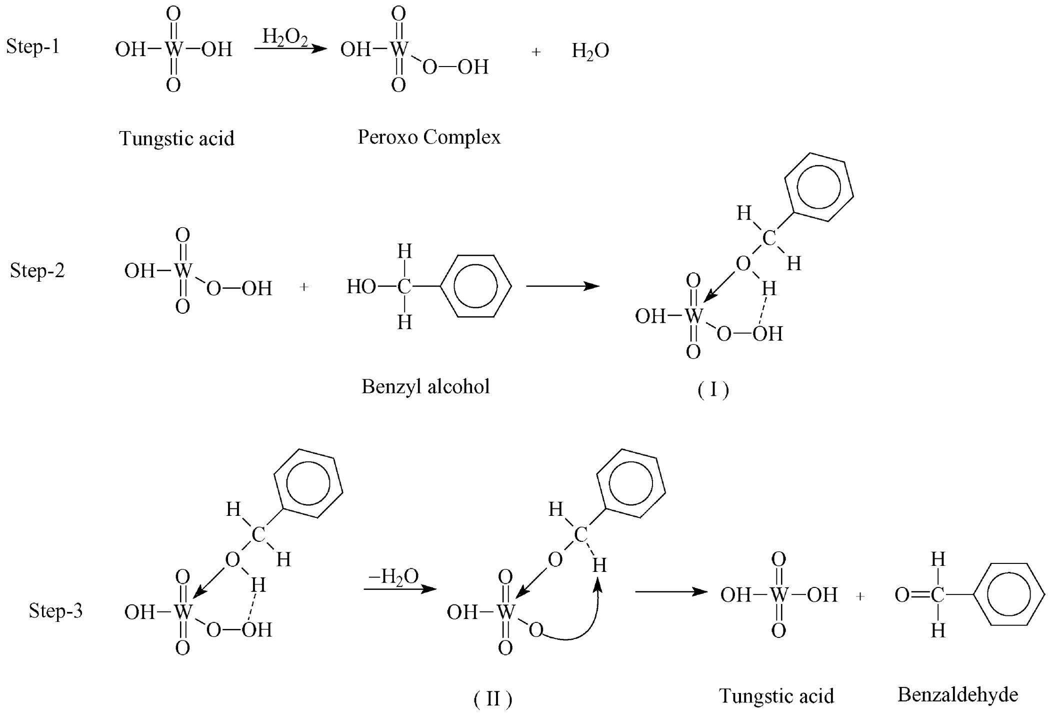

Fig. 6. Mechanism for oxidation of BzOH.

and tungstic acid, for the oxidation of BzOH is proposed (Fig. 6). In step-1, the peroxo complex is formed. In step-2, BzOH and peroxo complex react to give an intermediate I, which, on loss of the H_2O molecule, gives benzaldehyde and the regenerated catalyst (step-3).

Depending on the rates of mass transfer and relative rates of chemical reaction, Doraiswamy and Sharma [37] have classified the heterogeneous reactions as slow reactions and fast reactions, on the basis of value of $\sqrt{M}$ (ratio of the reaction in the film to the reaction in the bulk). For slow reactions, $\sqrt{M} \ll 1$. Further, in the slow reactions, there is a subclassification: (i) very slow reactions (kinetically controlled) and (ii) slow reactions (mass transfer controlled). For a reaction belonging to the latter case, the rate is influenced by the hydrodynamic conditions. While for the reaction falling in the former category reaction temperature normally influences the progress of the reaction significantly.

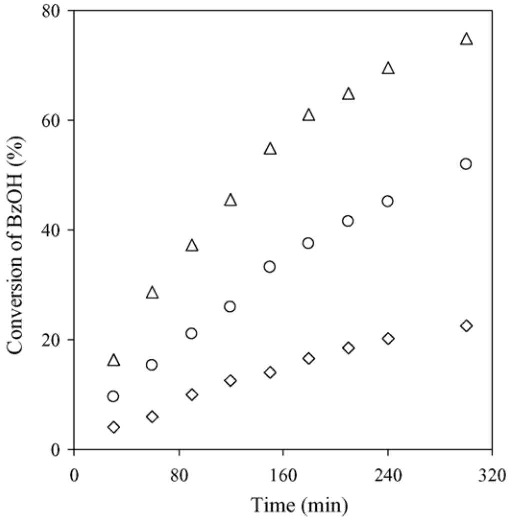

Fig. 7. Effect of reaction temperature on the conversion of BzOH (catalyst:ammonium molybdate). BzOH: 0.2 mol; H_2O_2: 0.2 mol; total aqueous phase: 122.6 mL; ammonium molybdate: 5.5×10^{-3} mol/L; (△) 363 K; (○) 353 K; (◊) 343 K.

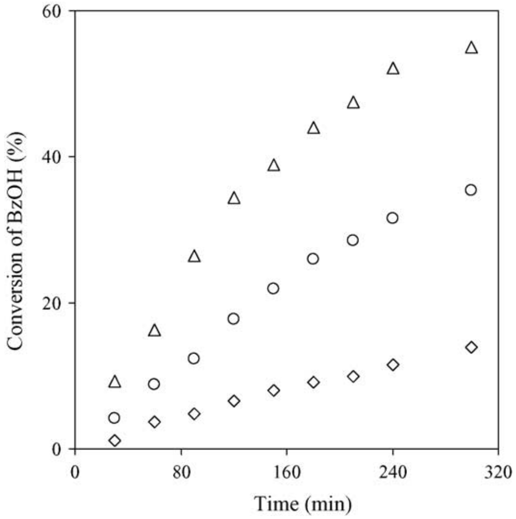

Fig. 8. Effect of reaction temperature on the conversion of BzOH (catalyst:tungstic acid). BzOH: 0.2 mol; H_2O_2: 0.2 mol; total aqueous phase: 122.6 mL; tungstic acid: 8.3×10^{-3} mol/L; (△) 363 K; (○) 353 K; (◊) 343 K.

The value of $\sqrt{M}$ evaluated for this system at 363 K (highest temperature) is 0.008, indicating the reaction is kinetically controlled. To ascertain the phase where reaction occurs, experiments were carried out at different volumes of aqueous phase, keeping initial hydrogen peroxide concentration constant. At constant hydrogen peroxide concentration, an increase in the volume of the aqueous phase gave a proportionate increase in the rate of the reaction, the volumetric rate of reaction remaining the same. The relative amount of the organic phase had no effect on the volumetric rate of the reaction. This indicates that the reaction occurs in the aqueous phase.

For a second-order reaction, in the present case, the rate equation is,

$$r_a = k[\text{catalyst}]\,[\text{alcohol}] \tag{2}$$

where r_a is the rate of consumption of benzyl alcohol, k the second-order rate constant, [catalyst] the catalyst concentration and [alcohol] is the concentration of benzyl alcohol.

$$r_a = k'C_A \tag{3}$$

where

$$k' = k[\text{catalyst}] \tag{4}$$

Eqn. (3) in the integrated form is

$$-\ln(1 - X_A) = k't \tag{5}$$

where X_A is conversion of BzOH at a batch time t. The linearity of plots in Figs. 9 and 10 indicate first-order dependence of oxidation rate on the concentration of BzOH.

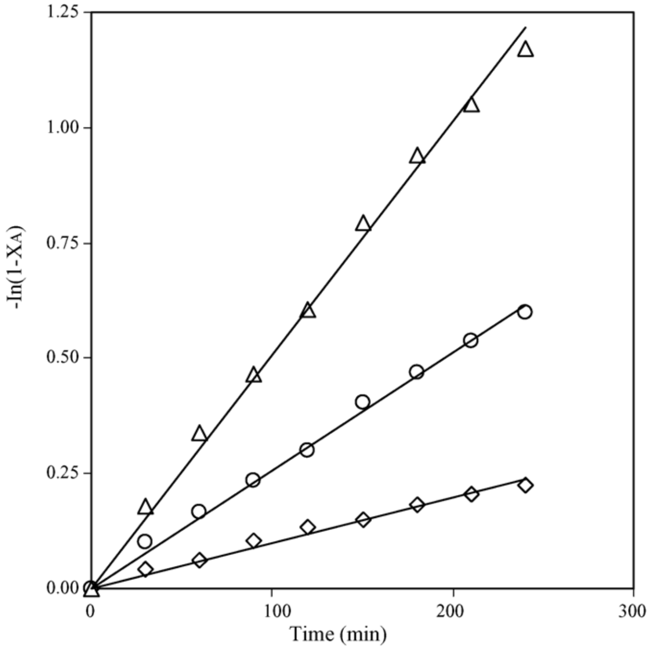

Fig. 9. Kinetic plots at different reaction temperatures (catalyst:ammonium molybdate). BzOH: 0.2 mol; H_2O_2: 0.2 mol; total aqueous phase: 122.6 mL; ammonium molybdate: 5.5×10^{-3} mol/L; (△) 363 K; (◯) 353 K; (◊)343 K.

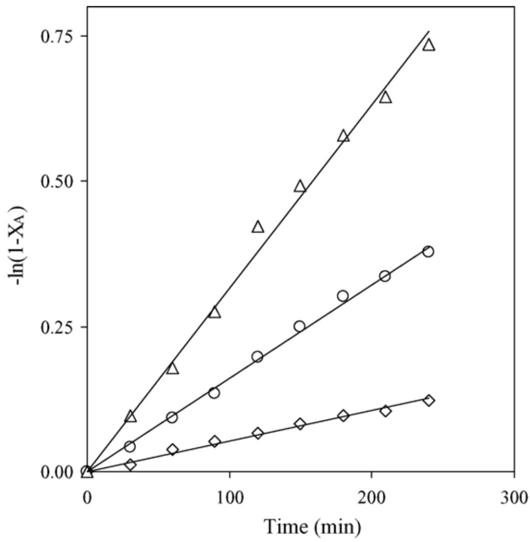

Fig. 10. Kinetic plots at different reaction temperatures (catalyst:tungstic acid). BzOH: 0.2 mol; H_2O_2: 0.2 mol; total aqueous phase: 122.6 mL; tungstic acid: 8.3×10^{-3} mol/L; (△) 363 K; (◯) 353 K; (◊) 343 K.

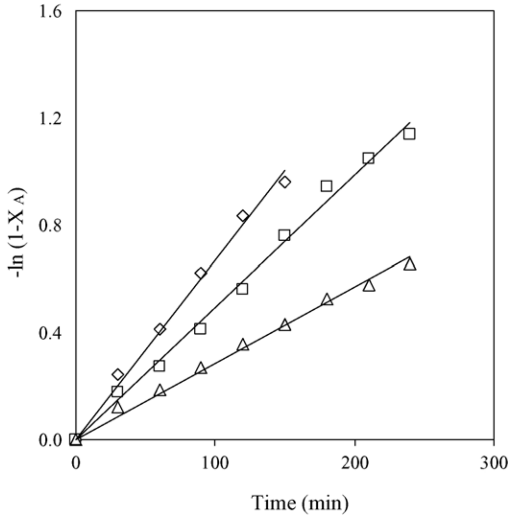

Fig. 11. Plot of $\ln(1-X_A)$ vs. time for different ammonium molybdate concentrations. BzOH: 0.2 mol; H_2O_2: 0.2 mol; total aqueous phase: 122.6 mL; temperature: 363 K; (◊) 8.3×10^{-3}mol/L; (□) 5.5×10^{-3} mol/L; (△) 3.4×10^{-3} mol/L.

Table 1

Catalyst	Temperature (K)		
	343	353	363
Ammonium molybdate			
$k' \times 10^3$ (min^{-1})[a]	1	2.4	5
$k \times 10^2$ (L mol^{-1} min^{-1})[b]	15	37	77
Tungstic acid			
$k' \times 10^3$ (min^{-1})[a]	0.5	1.5	2.7
$k \times 10^2$ (L mol^{-1} min^{-1})[b]	6	18	32

[a] Ammonium molybdate, 5.5×10^{-3} mol/L.

[b] Tungstic acid, 8.5×10^{-3} mol/L.

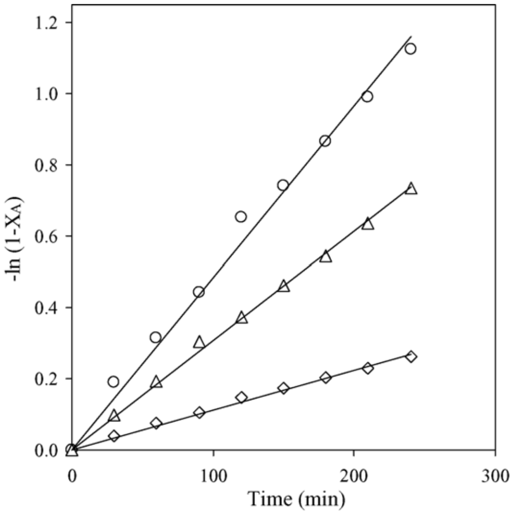

Fig. 12. Plot of $\ln(1-X_A)$ vs. time for different tungstic acid concentrations. BzOH: 0.2 mol; H_2O_2: 0.2 mol; total aqueous phase: 122.6 mL; temperature: 363 K; (◯) 15.9×10^{-3} mol/L; (△) 8.3×10^{-3} mol/L; (◊) 3.4×10^{-3} mol/L.

The values of the rate constant k' were calculated from the slope of the kinetic plots. (Figs. 9 and 10). Figs. 11–13 indicate, first-order dependence of the reaction rate on the catalyst concentration. The plot of k' against catalyst concentration [catalyst] was observed to be a straight line passing through the origin (Fig. 13). The values of k, second-order rate constant were calculated and are given in Table 1, together with values of k'. It was observed that k for ammonium molybdate is 2.5 times higher than the value of k for tungstic acid.

Thus, the reaction is directly proportional to the catalyst concentration and BzOH concentration. This indicates that the reaction between the peroxo complex and BzOH (step-2) (Fig. 6) is the rate-controlling step. Arrhenius plots for tungstic acid and ammonium molybdate are shown in Figs. 14 and 15. The values of the activation energy for oxidation of BzOH were 84 and 96 kJ/mol, for ammonium molybdate and tungstic acid as a catalyst, respectively.

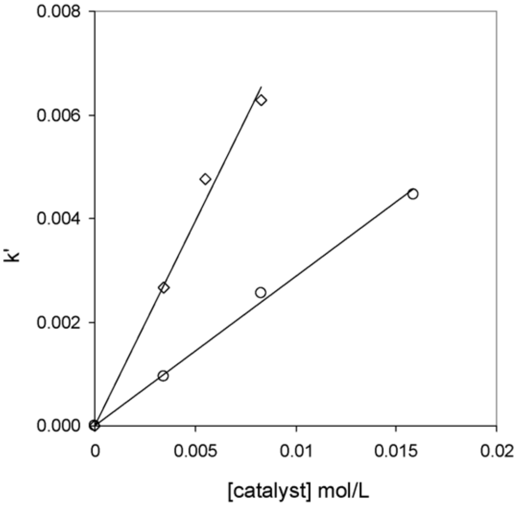

Fig. 13. Effect of catalyst concentration [catalyst] on the rate constant, k'. BzOH: 0.2 mol; H_2O_2: 0.2 mol; total aqueous phase: 122.6 mL; temperature: 363 K; (◊) ammonium molybdate (8.3–3.4) × 10^{-3} mol/L; (◯) tungstic acid (15.9–3.4) × 10^{-3} mol/L.

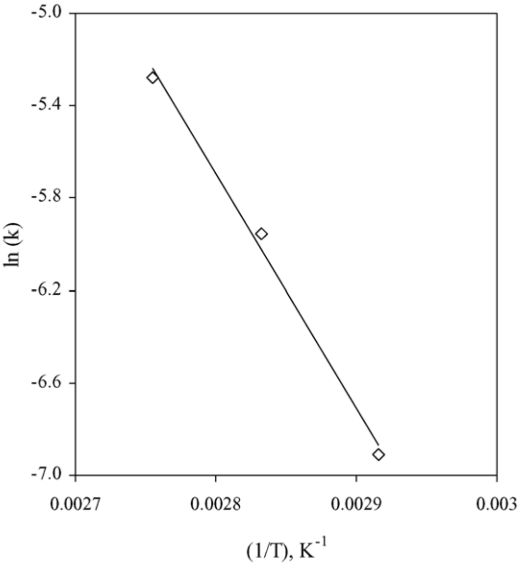

Fig. 14. Arrhenius plot for ammonium molybdate catalyst.

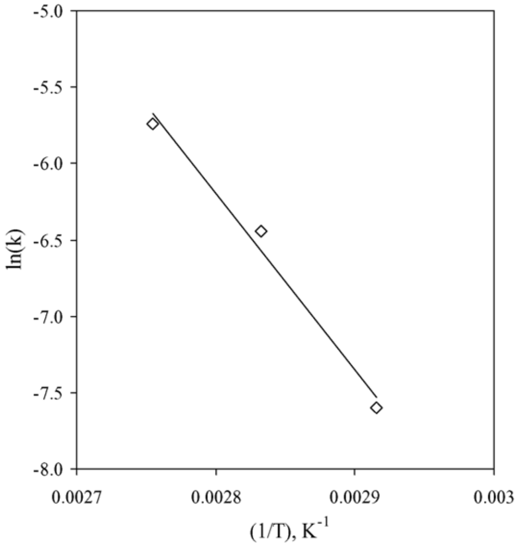

Fig. 15. Arrhenius plot for tungstic acid catalyst.

7. Conclusion

BzOH can be oxidized selectively to benzaldehyde, with hydrogen peroxide as an oxidizing agent and ammonium molybdate and tungstic acid as catalysts. The conversion of BzOH increases with increase in the catalyst concentration. Amongst the catalysts used, ammonium molybdate was found to be the best catalyst for oxidation of BzOH by H_2O_2.

The rate of reaction increases with increase in the reaction temperature. The reaction shows first-order dependance on the concentration of BzOH and the catalyst. The rate constant, *k*, observed to be 2.5 times more for ammonium molybdate comapared with tungstic acid. Values of activation energy for oxidation of BzOH are as 84 and 96 kJ/mol for ammonium molybdate and tungstic acid, respectively.

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