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# Kinetics and mechanism of selective hydroxylation of benzene catalysed by vanadium substituted heteropolymolybdates

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## Abstract

Hydroxylation of benzene to phenol was catalysed by vanadium substituted heteropolymolybdates of the general formula  $H_{3+x}[PMo_{12-x}V_xO_{40}] \cdot nH_2O$  where,  $x = 1, 2, 3$ . The optimum catalytic activities (TON = 50–90) were found, when the reaction was performed with equimolar ratio of substrate to oxidant (hydrogen peroxide) at 338 K. Kinetic investigations of the reaction catalysed by mono vanadium substituted heteropolymolybdates, revealed a first-order dependence with respect to the concentrations of the substrate and the catalyst and a half-order dependence with respect to concentration of the oxidant. Temperature dependence on the rate of hydroxylation was also studied and from Arrhenius plot, the activation energy was evaluated to be  $21.5 \text{ kcal mol}^{-1}$ . In situ UV–VIS and electron paramagnetic resonance (EPR) spectroscopic studies were carried out to establish the active species. A mechanism involving vanadium (V) peroxo intermediate species has been proposed for the hydroxylation of benzene to phenol. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Hydroxylation of benzene; Heteropolymolybdates; Catalysis; Spectroscopy; Kinetics

## 1. Introduction

Phenol is produced mainly by Hock process, in which cumene is oxidized to cumenehydroperoxide by air oxidation in aqueous emulsion ( $Na_2CO_3$ ) and its subsequent cleavage in acidic media to equimolar amounts of phenol and acetone [1]. The economy of this process is strongly dependent on the market price of the side product acetone. Therefore, efforts are in progress for the development of a new route towards phenol synthesis by a one-stage process via hydroxylation of benzene to phenol. Hence, hydroxylation of

benzene to phenol in a single-stage has remained as an intriguing reaction and much research work has been focused on the development of catalyst systems for this purpose.

Many transition metal containing catalytic systems have been tried for the hydroxylation of benzene to phenol and so far no appreciable success has been achieved. In recent years, there has been a considerable interest in transition metal substituted polyoxometalates as catalysts for the oxidation of organic substrates. Literature survey reveals that transition metal substituted polyoxometalates (TMSP) and mixed addenda polyoxometalate complexes were found to be good catalysts for the oxidation of a large variety of organic substrates [2]. The guest transition metal atoms act as efficient oxygen transfer agent.

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Iron and chromium containing phosphotungstate salts have also been reported by Kuznetsova et al. as efficient catalysts for benzene hydroxylation with hydrogen peroxide as an oxidant [3,4]. Various other catalytic systems involving heteropoly complexes have been employed for this reaction [5–8]. Vanadium substituted phosphotungstates and phosphomolybdates were also reported as catalysts for phenol production under various reaction conditions [9–11]. However, benzene conversions reported for hydroxylation of benzene to phenol in the literature were very low under the specified reaction conditions. This prompted us to modify the reaction conditions to improve yields of phenol formation.

In this paper, we are reporting our findings on the catalytic activities of molybdovanadophosphoric acid series of catalysts having the general formula  $H_{3+x}[PMo_{12-x}V_xO_{40}] \cdot nH_2O$  where,  $x = 1, 2, 3$  in the hydroxylation of benzene to phenol with hydrogen peroxide as an oxidant. Optimum reaction conditions evaluated under homogeneous reaction conditions for the hydroxylation of benzene to phenol were equimolar ratio of substrate to oxidant (hydrogen peroxide) at 338 K in acetonitrile solvent.

## 2. Experimental

### 2.1. Materials

$Na_2HPO_4 \cdot 12H_2O$ ,  $Na_2MoO_4 \cdot 2H_2O$ ,  $NaVO_3$ , (M/s Loba Chemicals, India), concentrated  $H_2SO_4$  and diethylether were used as received for the preparation of molybdovanadophosphoric acids. Benzene, aqueous 30% hydrogen peroxide (E. Merck, India Ltd., India), acetonitrile of high purity grade were used as such without further purification. Strength of hydrogen peroxide was determined by redox titration with  $KMnO_4$  prior to use in the oxidation reaction. Phosphomolybdic acid was used as such.

### 2.2. Catalysts preparation

The mono-, di- and tri-vanadium substituted phosphomolybdic acids were prepared by following the synthesis methods developed by Tsigdinos and Hallada [12]. These acids were prepared by mixing the aqueous solutions of  $Na_2HPO_4 \cdot 12H_2O$ ,  $NaVO_3$  and

$Na_2MoO_4 \cdot 2H_2O$  in appropriate molar ratio in acidic medium. The heteropoly acids formed were extracted with diethylether and recovered by evaporation of ether layer. The resulting orange coloured powders were recrystallised from water and the crystals were dried in air and stored over silica gel in a desiccator. These crystals were finely powdered and used in the hydroxylation of benzene.

### 2.3. Apparatus and instrumentation

The infrared spectra of the freshly prepared catalysts were recorded on a Shimadzu FTIR 8201 PC instrument as nujol mulls at 298 K between 4000 and  $400\text{ cm}^{-1}$  region. Thermal analysis of the samples were performed on a Seiko model instrument (TG/DTA32) and the measurements were done at a heating rate of  $10\text{ K min}^{-1}$  from 303 to 873 K under nitrogen atmosphere. The electronic spectra of the catalysts in acetonitrile were recorded at 298 K on a Shimadzu UV-2101 PC UV-VIS spectrophotometer in the region 260–540 nm. The EPR spectra were recorded on a Bruker EMX-X band spectrometer with 100 kHz field modulation. Measurements were performed on powder samples and their acetonitrile solutions at 77 and 298 K. The spin Hamiltonian parameters were determined by simulating the spectra using a Bruker Simfonia software package.

### 2.4. Catalytic testing and product analysis

The oxidation reactions were carried out in a two-necked 50 ml round bottom flask placed in an oil bath maintained at 338 K. In a typical experiment, 0.05 g (0.025 mM) of catalyst, 1.56 g (20 mM) of benzene and 2.36 g (20 mM) of aqueous hydrogen peroxide were mixed in 6 ml of acetonitrile and placed in the flask and the contents were stirred with a magnetic stirrer. The reaction mixtures withdrawn at regular interval of 30 min were analysed by gas chromatography (Hewlett Packard gas chromatograph model No. 5890 Series-II) using HP-5 fused column with  $30\text{ m} \times 0.53\text{ mm} \times 1.0\text{ }\mu\text{m}$  film thickness and FID detector. Phenol formed in the reaction was confirmed by comparing the retention time (standard) and also by GCMS. From the moles of benzene reacted, turnover numbers were calculated. The samples were also analysed simultaneously by UV-VIS and

EPR spectroscopy to identify the active intermediate species.

### 3. Results and discussion

#### 3.1. Catalyst characterisation

The acid strength of  $H_4[PMo_{11}VO_{40}] \cdot nH_2O$  was determined by pH metry [12]. Methanolic solution of the catalysts (25 ml, 0.002 M) were titrated against 0.0024 M sodium methoxide solution. The change in the pH with the addition of a base was measured by a pH meter and these values were then plotted as pH versus ml of base added. After the determination of the neutralisation point, the acid was found to be tetraprotic with four replaceable hydrogen atoms.

The infrared spectra of the freshly prepared catalysts exhibited typical skeletal vibrations of the Keggin oxoanion in the region 1100–700  $cm^{-1}$ . The major peaks at 1060, 960 and 865 and 780  $cm^{-1}$  are attributed to  $\nu(P-O_i-Mo)$ ,  $\nu(Mo-O_t)$  and  $\nu(Mo-O_b-Mo)$ , respectively. Here  $O_i$ ,  $O_t$  and  $O_b$  are the inner, terminal and bridging oxygen atoms, respectively, in the Keggin anionic framework. Total water content in the catalysts was determined by thermal analysis. The final compositions of the catalysts were found to be  $H_4[PMo_{11}VO_{40}] \cdot 20H_2O$ ,  $H_5[PMo_{10}V_2O_{40}] \cdot 15H_2O$  and  $H_6[PMo_9V_3O_{40}] \cdot 17H_2O$ . The mono-, di- and tri-vanadium substituted acids, henceforth, will be referred to as  $PMo_{11}V$ ,  $PMo_{10}V_2$  and  $PMo_9V_3$ , respectively, in the remaining part of the text.

The UV–VIS spectra of the catalysts in acetonitrile showed absorption maximum at 307 nm. This band at 307 nm is associated with octahedrally coordinated  $Mo^{6+}$  and arises due to ligand to metal charge transition [13]. The presence of vanadium in the Keggin structure has broadened the LMCT band.

Vanadium substituted heteropolymolybdates  $PMo_{11}V$ ,  $PMo_{10}V_2$  and  $PMo_9V_3$  showed EPR spectra typical of a vanadium(IV) ion [14]. The spectra of solid samples were broad due to spin–spin interactions and the  $CH_3CN$  solution spectra showed eight narrow signals ( $\Delta H_{pp} = 12$  G). These signals arose due to the interaction of unpaired electron spin ( $S = 1/2$ ) with the nuclear spin of vanadium ( $^{51}V$  has a nuclear spin  $I = 7/2$  with a natural abundance

of 99.75%). The separation between the adjacent hyperfine signals is not equal due to second-order interactions and increases from 105 to 129.5 G in increasing field direction. The isotropic  $g$  and hyperfine coupling constants were estimated to be 1.965 and 117 G, respectively. The spectra for frozen  $CH_3CN$  solutions, at 77 K, were almost similar for all the three vanadium containing catalysts and were characterised by an axial  $g$  and hyperfine tensors ( $g_{\parallel} = 1.933$ ,  $g_{\perp} = 1.977$ ,  $A_{\parallel} = 202.0$  G and  $A_{\perp} = 76.7$  G).  $PMo_{10}V_2$  and  $PMo_9V_3$  samples did not reveal the presence of multinuclear vanadium centres.

The acid–base titrations indicated the oxidation state of vanadium to be +5. In such a case the sample should have been EPR inactive. On the contrary, we found the samples to be paramagnetic and showed EPR signals corresponding to the +4 oxidation state of vanadium. These results, therefore, suggests that a small quantity of vanadium is probably present as  $VO^{2+}$  ion outside the keggin structure compensating for two  $H^+$  ions. Bayer et al. have reported the formation of  $(VO)^{2+}H_2[PMo_{11}V]$  during the synthesis of  $PMo_{11}V$  [15]. In our samples the former type is probably present at impurity levels. EPR spectroscopy being a sensitive technique for paramagnetic ions has detected these impurity species. Vanadium substituted for molybdenum ions, in the keggin structure is in +5 oxidation state.

#### 3.2. Catalytic activity

The catalytic activities of vanadium substituted phosphomolybdic acids were investigated in the hydroxylation of benzene to phenol and the results are presented in Table 1. The hydroxylation of benzene gave phenol as the only product under the reaction conditions studied.

Table 1  
Catalyst activities in hydroxylation of benzene to phenol<sup>a</sup>

Catalyst	Benzene conv. (mol%)	TON
$PMo_{11}V$	10.7	92
$PMo_{10}V_2$	9.2	74
$PMo_9V_3$	6.3	50

<sup>a</sup> Conditions: benzene (0.02 M),  $H_2O_2$  (0.02 M), catalyst (0.05 g), acetonitrile (6 ml), temperature (338 K), reaction time (2 h) and TON — turnover number (moles of benzene converted per mole of catalyst).

The maximum conversion of benzene ( $\cong 11\%$ ) with  $\text{TON} = 92$  was achieved with  $\text{PMo}_{11}\text{V}$ . However, when the hydroxylation was carried out with free phosphomolybdic acid, no hydroxylation activity was seen. This confirms that vanadium is the active centre in the above catalysts. The conversion of benzene increases linearly with all the catalysts and then becomes stable with further no change in the activities of catalysts. It is found that the activities of the three catalysts in hydroxylation of benzene to phenol decreased in the following order.



In other words, the catalytic activity for hydroxylation of benzene decreased with the number of vanadium centres in the polyoxoanion system. The catalyst activities data indicated that  $\text{PMo}_{11}\text{V}$  was comparatively more active than di- and tri-vanadium substituted catalysts. The decrease in the catalytic activity of the di- and tri-vanadium substituted catalysts could be due to the poor stabilities of the corresponding peroxo intermediate species in the oxygen transfer reaction.

### 3.3. Kinetics of hydroxylation of benzene to phenol catalysed by $\text{PMo}_{11}\text{V}$

Hydroxylation of benzene catalysed by  $\text{PMo}_{11}\text{V}$  under the reaction conditions studied gave phenol. Hence, kinetic investigations of this reaction were carried out to establish the dependence of rate of hydroxylation with respect to the variations in the concentrations of the reactants involved in the system in excess acetonitrile solvent. The total volume of the reaction mixture in all kinetic experiments was adjusted to 10 ml by the addition of acetonitrile solvent. Rates of hydroxylation of benzene were calculated from the plots of moles of benzene reacted versus time.

#### 3.3.1. Effect of substrate concentration

Experiments on hydroxylation of benzene were carried out at 338 K by varying the concentrations of the substrate benzene (0.01–0.04 M), while keeping the concentrations of  $\text{H}_2\text{O}_2$  (0.02 M) and catalyst ( $2.33 \times 10^{-5}$  M) constant. The effect of substrate concentration on the rate of hydroxylation of benzene is shown in Fig. 1(a), as a plot of rate versus concentration of benzene. It was found that the rate of hydroxylation

of benzene to phenol showed a first-order dependence with respect to substrate concentration.

#### 3.3.2. Effect of $\text{H}_2\text{O}_2$ (oxidant) concentration

Keeping substrate as 0.02 M, catalyst,  $2.33 \times 10^{-5}$  M and temperature, 338 K constant, the  $\text{H}_2\text{O}_2$  concentration was varied between 0.02 and 0.1 M. The graph of rate of hydroxylation versus  $[\text{H}_2\text{O}_2]^{-1/2}$  (Fig. 1(b)) is linear and showed a half-order dependence with respect to oxidant concentration. In other words, half a mole of oxygen is transferred from oxidant to benzene to give phenol.

#### 3.3.3. Effect of catalyst concentration

Catalyst concentration was varied between 0.75 and  $2.33 \times 10^{-5}$  M, at substrate, 0.02 M, oxidant, 0.1 M and temperature 338 K. Fig. 1(c) shows the graph of rate of hydroxylation versus catalyst concentration and it is seen from the graph that the rate of hydroxylation has a linear and first-order dependence with respect to catalyst concentration.

#### 3.3.4. Effect of temperature

Effect of temperature on the rate of hydroxylation of benzene to phenol was studied by varying the temperature between 310 and 338 K, while other parameters were kept constant as substrate, 0.02 M, oxidant, 0.02 M and catalyst,  $2.33 \times 10^{-5}$  M. From Arrhenius plot of  $\ln k$  versus  $1/T$  shown in Fig. 1(d), the activation energy  $E_a$  evaluated was  $21.5 \text{ kcal mol}^{-1}$ .

In order to understand the transient species formed during the course of the above reaction, the reaction mixtures were subjected to UV–VIS and EPR spectroscopic studies at regular time intervals.

### 3.4. UV–VIS spectroscopy

A fixed volume of the reaction mixture diluted with acetonitrile was studied by absorption spectroscopy at regular time interval of 30 min. Upon the addition of the oxidant and substrate to the catalyst solution, the UV–VIS spectra showed the appearance of a new band at 330 nm in addition to the already existing band at 307 nm. This new band at 330 nm could be due to the formation of vanadium (V) peroxo species, which is an active intermediate, formed as a result of interaction of the vanadium centre with hydrogen peroxide. The intensity of this band increased lin-

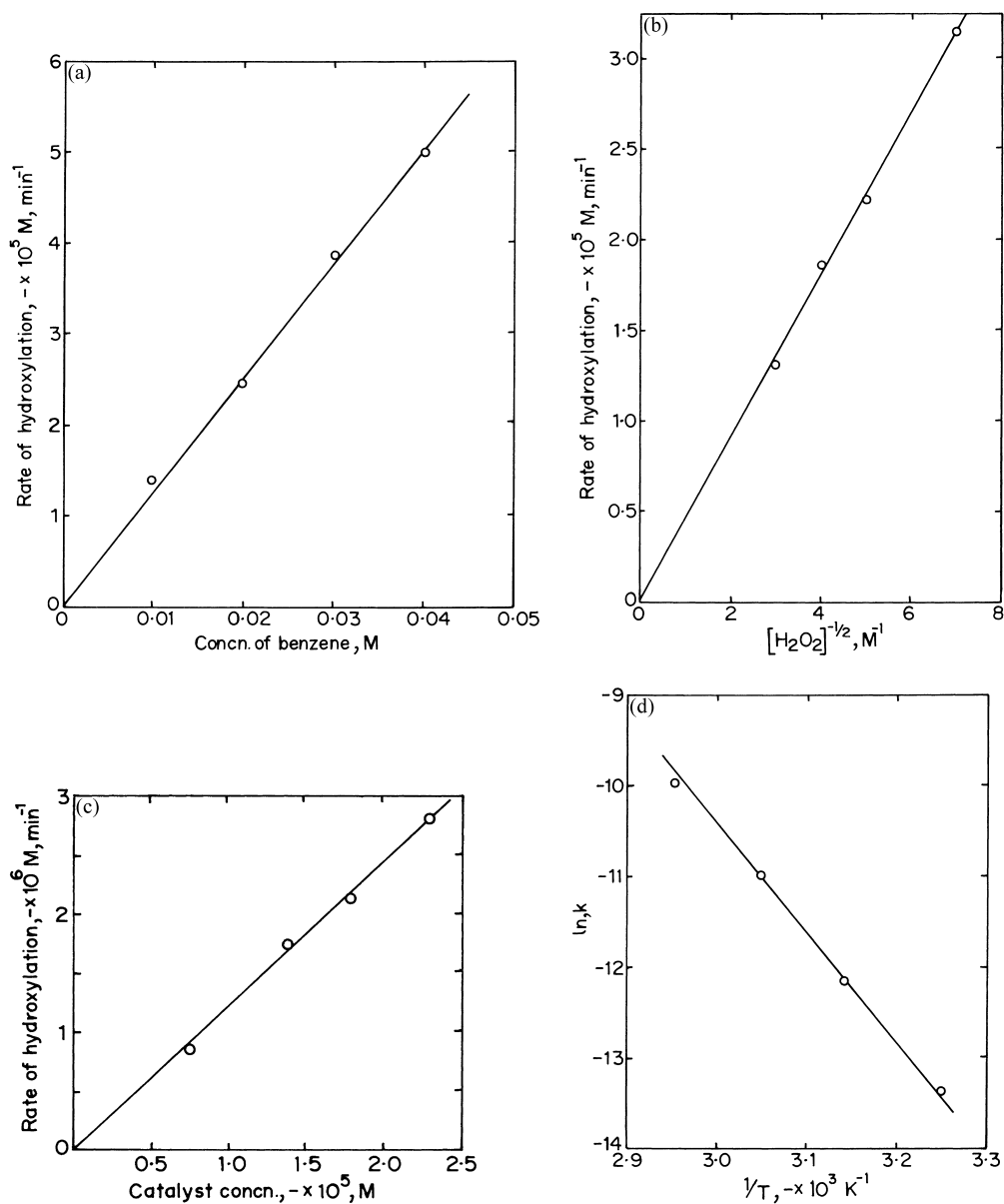


Fig. 1. (a) Effect of substrate concentration; (b) effect of oxidant concentration; (c) effect of catalyst concentration, and (d) Arrhenius plot.

early during the course of the reaction. This increase in intensity is an indication of phenol formation and simultaneous  $\text{H}_2\text{O}_2$  decomposition in the system. The intensity then reduced and the concentration of phenol remained constant in the course of the reaction. This was verified by gas chromatographic analysis. Fig. 2

shows the UV–VIS spectral changes for the reaction mixture containing  $\text{PMo}_{11}\text{V}$ . Similar pattern was observed, when the di- and tri-vanadium substituted catalysts were used. Active intermediate species were formed in all the three catalysts but their stabilities were found to be different. The active species formed

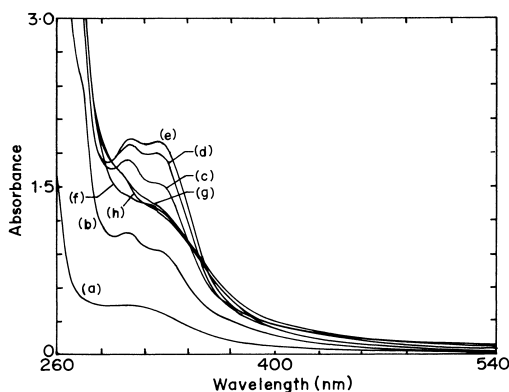


Fig. 2. Absorption spectra of  $\text{PMo}_{11}\text{V}$  as a function of time.  $[\text{HPA}] = 2.33 \times 10^{-5} \text{ M}$ ;  $[\text{C}_6\text{H}_6] = 0.02 \text{ M}$ ;  $[\text{H}_2\text{O}_2] = 0.02 \text{ M}$ ;  $T = 65^\circ\text{C}$ . (0.075 g of sample diluted to 10 ml with acetonitrile): (a) 0 min; (b) 30 min; (c) 60 min; (d) 90 min; (e) 120 min; (f) 150 min; (g) 180 min, and (h) 210 min.

by mono vanadium substituted phosphomolybdic acid was more stable than the other two. This observation supported the fact that only a single vanadium site ( $\text{PMo}_{11}\text{V}$ ) is needed for hydroxylation reaction [11].

### 3.5. EPR spectroscopy

EPR spectroscopy is used to monitor the paramagnetic transient species formed during benzene hydroxylation by vanadium substituted heteropolymolybdates. This technique revealed the role of vanadium in the catalytic hydroxylation of benzene. A known amount of the sample was taken out each time from the reaction mixture at specified times and spectra were recorded after quenching the samples to 298 and 77 K, respectively. Representative spectra for the reaction mixture containing the catalyst  $\text{PMo}_{11}\text{V}$  at different reaction times is shown in Fig. 3. The spectral variations for all the three catalysts are, in general, similar. The  $\text{CH}_3\text{CN}$  solutions without  $\text{H}_2\text{O}_2$  are paramagnetic due to trace quantities of  $\text{VO}^{2+}$  as the counter cation (species I; Fig. 3(a)). Soon after adding  $\text{H}_2\text{O}_2$ , the solutions became EPR silent due to the oxidation of  $\text{V(IV)}$  to  $\text{V(V)}$  (Fig. 3(b)). After a certain time, signals corresponding to two new vanadium(IV) species I' and II appeared (Fig. 3(c)). The Hamiltonian parameters of these species are different ( $g_{\text{iso}} = 1.970$ ,  $A_{\text{iso}} = 108.2 \text{ G}$  for species I' and  $g_{\text{iso}} = 1.963$  and  $A_{\text{iso}} = 95.2 \text{ G}$  for species II)

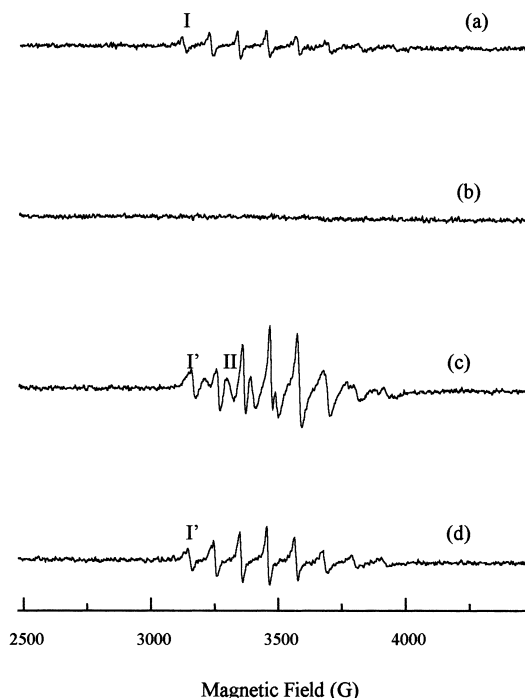


Fig. 3. Room temperature EPR spectra of  $\text{PMo}_{11}\text{V}$  in the reaction mixture as a function of time: (a)  $\text{PMo}_{11}\text{V}$  + benzene +  $\text{CH}_3\text{CN}$ ; (b) reaction mixture +  $\text{H}_2\text{O}_2$  at 0 min; (c) 90 min, and (d) 24 h.

from those of original species I ( $g_{\text{iso}} = 1.965$  and  $A_{\text{iso}} = 117.0 \text{ G}$ ). A lower value for  $A_{\text{iso}}$ , especially for species II reveals lower symmetry at the site of vanadium and higher delocalisation of electron density onto the ligands. The intensity of the signals for species I' and II was maximum at a reaction time of 90 min for  $\text{PMo}_{11}\text{V}$ , 60 min for  $\text{PMo}_{10}\text{V}_2$  and 30 min for  $\text{PMo}_9\text{V}_3$  catalyst systems and then onwards, signals of species II decreased and finally disappeared. Variation of log intensities of signals for species I' and II for all the three catalysts are shown in Fig. 4. While the behaviour of intensity variation is similar for  $\text{PMo}_{10}\text{V}_2$  and  $\text{PMo}_9\text{V}_3$  this variation for the catalyst system  $\text{PMo}_{11}\text{V}$  is different, especially for species I'. This signal intensity of species I' for  $\text{PMo}_{10}\text{V}_2$  and  $\text{PMo}_9\text{V}_3$  increased gradually and reached a maximum value while that for  $\text{PMo}_{11}\text{V}$  decreased with time. The spectra after 24 h contained signals due to species I' only (Fig. 3(d)). The overall spectral intensity of the vanadium(IV) ion increased at the end of the reaction and suggests that a part of the substituted vanadium

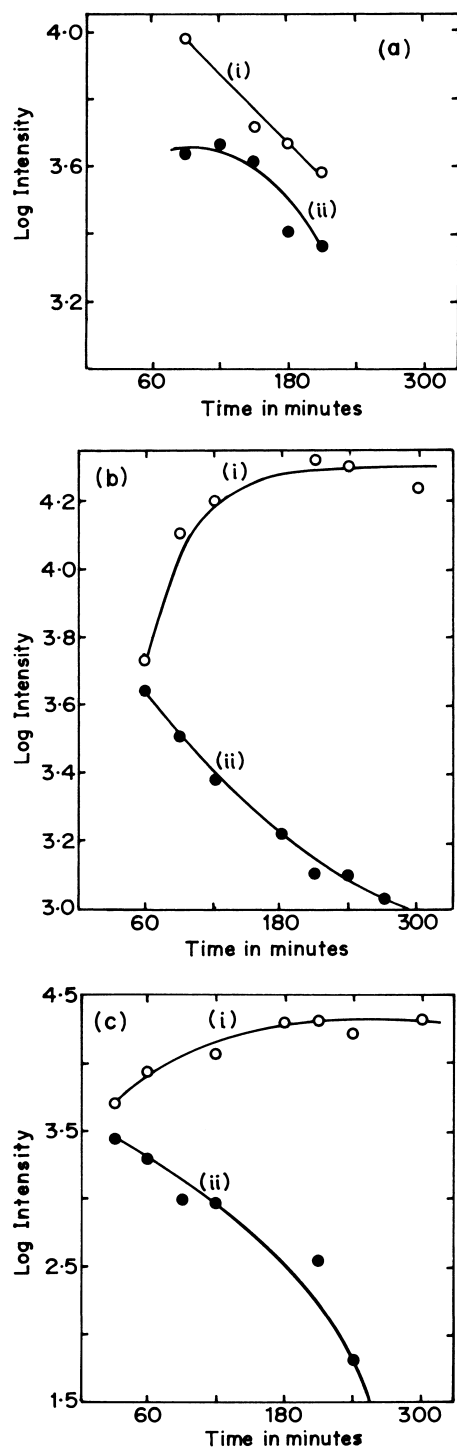


Fig. 4. Plot showing the variation of EPR signal intensity for species I' (i) and species II (ii) as a function of time: (a) PMo<sub>11</sub>V; (b) PMo<sub>10</sub>V<sub>2</sub>, and (c) PMo<sub>9</sub>V<sub>3</sub>.

leaches out during the course of the reaction. This leaching for catalysts PMo<sub>10</sub>V<sub>2</sub> and PMo<sub>9</sub>V<sub>3</sub> is more and thus shows a different type of intensity variation for species I'. It is interesting to note that molybdenum centre is not involved in the hydroxylation reaction.

### 3.6. Mechanism and rate law

Based on the spectroscopic and kinetic observations made in the system, a mechanism has been proposed for vanadium substituted heteropoly acid catalysed hydroxylation of benzene to phenol and is shown in Scheme 1.

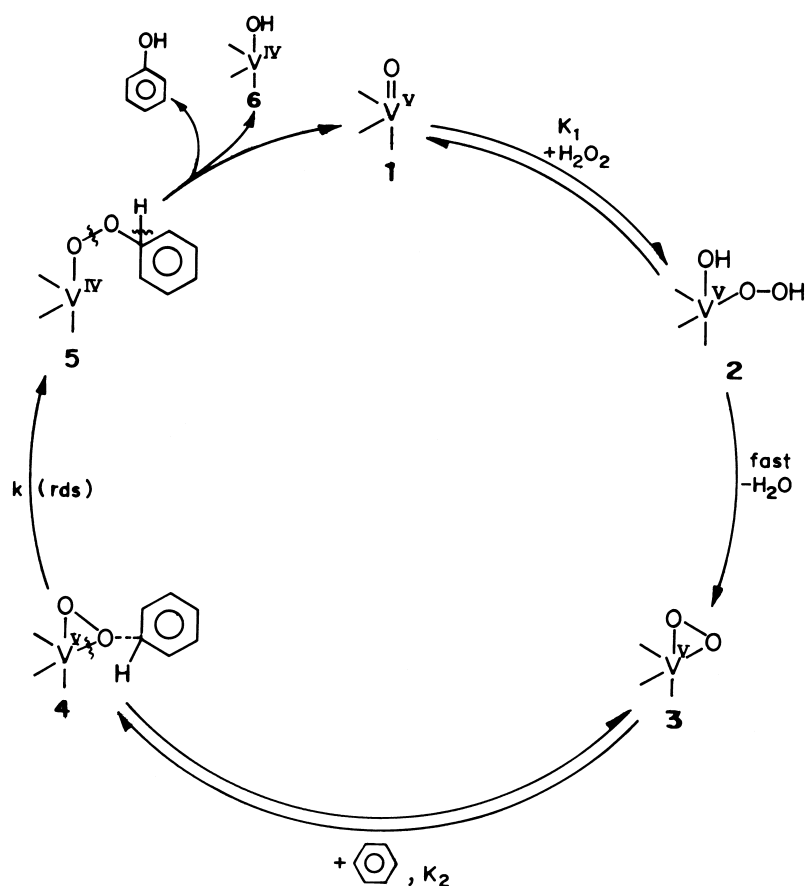
The proposed mechanism involves the transformation of vanadium in heteropolymolybdates to an unstable vanadium (V) hydroxy hydroperoxy species **2**, on interaction with hydrogen peroxide in a preequilibrium step. Species **2**, rapidly transforms into a relatively stabler vanadium (V) peroxy species **3** on loss of a water molecule. This species has been identified and shows a band at 330 nm in the UV–VIS spectra. The species **3**, interacts with the substrate benzene in another preequilibrium step to give a metallo-peroxy-arene intermediate species **4**. Transfer of oxygen by C–H bond activation takes place in a rate determining step (RDS) to give vanadium(IV) phenoxy intermediate species **5**. The species **5** has been identified as species II in the EPR spectrum (Fig. 3(c)). Homolytic cleavage in species **5** results in rapid dissociation to give phenol and regenerating the species **1** and a small amount of vanadium(IV) hydroxo species **6**, in a catalytic cycle. Species **6** has been identified as a stable species I' in the EPR spectrum. The built in concentration of inactive species **6** reduced the catalytic activity in the system.

Based on the Scheme 1 and kinetic rate dependence studies, the rate law for PMo<sub>11</sub>V catalysed hydroxylation of benzene to phenol could be written as

$$\text{rate} = kK_1K_2[\text{HPA-V}][\text{S}][\text{H}_2\text{O}_2]^{1/2} \quad (1)$$

where  $k$  is the over all rate constant of the reaction,  $K_1$  and  $K_2$  are preequilibrium constants as shown in Scheme 1, [HPA–V] is the PMo<sub>11</sub>V catalyst concentration, [S] the benzene concentration and [H<sub>2</sub>O<sub>2</sub>] is the hydrogen peroxide concentration.

By applying steady state reaction conditions and the total concentration of catalyst present in different



Scheme 1.

forms (shown in Scheme 1) is expressed as  $[\text{HPA-V}]_T$ , then the rate law can be modified as

$$\text{rate} = \frac{kK_1K_2[\text{HPA-V}]_T[\text{S}][\text{H}_2\text{O}_2]^{1/2}}{1 + K_1[\text{H}_2\text{O}_2]^{1/2} + K_1K_2[\text{S}][\text{H}_2\text{O}_2]^{1/2}} \quad (2)$$

To evaluate equilibrium and kinetic constants graphically, Eq. (2) could be rearranged in a slope and intercept form in the following two ways:

$$\frac{[\text{HPA-V}]_T}{\text{rate}} = \frac{1}{[\text{S}]} \left( \frac{1}{kK_1K_2[\text{H}_2\text{O}_2]^{1/2}} + \frac{1}{kK_2} \right) + \frac{1}{k} \quad (3)$$

$$\frac{[\text{HPA-V}]_T}{\text{rate}} = \frac{1}{[\text{H}_2\text{O}_2]^{1/2}} \left( \frac{1}{kK_1K_2[\text{S}]} \right) + \frac{1}{k} \left( 1 + \frac{1}{K_2[\text{S}]} \right) \quad (4)$$

From Eq. (3), a plot of  $[\text{HPA-V}]_T/\text{rate}$  versus  $1/[\text{S}]$  gives a straight line with an intercept from which, the value of  $k$  was calculated. Similarly from Eq. (4), a plot of  $[\text{HPA-V}]_T/\text{rate}$  versus  $1/[\text{H}_2\text{O}_2]^{1/2}$  gives a straight line and substituting the value of  $k$ , in the slope and intercept values of this graph, the preequilibrium constants  $K_1$  and  $K_2$  were obtained. Thus, the values of  $k$ ,  $K_1$ ,  $K_2$  for the hydroxylation of benzene to phenol catalysed by  $\text{PMo}_{11}\text{V}$  at 338 K were found to be as  $k = 8.33 \text{ min}^{-1}$ ,  $K_1 = 39.4 \text{ M}^{-1}$  and  $K_2 = 2.63 \text{ M}^{-1}$ , respectively.

From the temperature dependence study carried out on hydroxylation of benzene to phenol, the energy of activation was evaluated. Other thermodynamic activation parameters, such as, enthalpy of activation ( $\Delta H^\ddagger$ ), entropy of activation ( $\Delta S^\ddagger$ ) and free energy of activation ( $\Delta G^\ddagger$ ) were calculated from standard



thermodynamic equations. These values are,  $E_a = 21.5 \text{ kcal mol}^{-1}$ ,  $\Delta H^\ddagger = 20.9 \text{ kcal mol}^{-1}$ ,  $\Delta S^\ddagger = 48.1 \text{ cal } ^\circ\text{C}^{-1} \text{ mol}^{-1}$  and  $\Delta G^\ddagger = +5.37 \text{ kcal mol}^{-1}$ .

#### 4. Summary

The catalytic activities of vanadium containing heteropolymolybdates of the general formula  $\text{H}_{3+x}[\text{PMo}_{12-x}\text{V}_x\text{O}_{40}] \cdot n\text{H}_2\text{O}$  where,  $x = 1, 2, 3$  in the selective hydroxylation of benzene were investigated using hydrogen peroxide as oxidant. GC analysis revealed phenol as the only product of oxidation. The effects of various parameters like temperature, the concentrations of substrate, catalyst and oxidant on the rate of hydroxylation of benzene were studied and thermodynamic activation parameters were estimated. The UV–VIS and EPR spectroscopic techniques were used to monitor the active intermediate species. A mechanism of hydroxylation reaction involving vanadium (V) peroxo intermediate species has been proposed.

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