

A Comparative Study of Catalysis by Zeolite Encapsulated and Neat Copper *o*-Phenylenediamine Complexes towards Oxidation of Catechol and 3,5-di-*tert*-Butylcatechol Using Hydrogen Peroxide¹

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Abstract—The kinetics of hydrogen peroxide oxidation of catechol (CAT) and 3,5-di-*tert*-butylcatechol (DTBC) using neat as well as zeolite encapsulated copper complexes of *o*-phenylenediamine as catalysts have been investigated by a novel UV-visible spectrophotometric technique. The order with respect to the substrate, hydrogen peroxide, as well as the catalyst was unity for all the reactions. This indicates that the mechanism of the reaction is unaltered by encapsulation of the complex although considerable difference exists in the rate of catalysis. The effects of polarity and pH on the reaction were found to be different for the four reactions, suggesting the existence of a deprotonation equilibria for the catalysts in addition to those for the substrates. The rate of oxidation of DTBC was more than that of catechol in the presence of both the catalysts signifying that the inductive effect dominates over the steric constraints in this case. The present work allowed the determination of the acid dissociation constants of Cu(OPD)₂ and YCu(OPD)₂ in 1 : 9 methanol–water mixtures.

INTRODUCTION

Many attempts are being made to synthesize metal complexes that model biological systems and to reproduce the structural, spectroscopic, and reactivity properties of enzymes [1–5]. We have recently synthesized various supported as well as neat complexes of cobalt(II), nickel(II), and copper(II) and screened their catalytic activity towards the oxidation of catechol to *o*-benzoquinone [6]. Among these complexes, the supported copper complex of *o*-phenylenediamine (YCu(OPD)₂) was found to exhibit the highest catalytic activity. Tyrosinase, a metalloenzyme known to be a biological catalyst for the same reaction, also contains copper atoms [7, 8]. It was therefore found worthwhile to investigate the kinetics and mechanism of catechol oxidation to *o*-benzoquinone by hydrogen peroxide using the zeolite-encapsulated as well as neat copper(II) complex of *o*-phenylenediamine as the catalysts. We have also studied the kinetics of oxidation of 3,5-di-*tert*-butylcatechol in the presence of the above two catalysts for the sake of comparison. The results of these studies are presented in this paper.

EXPERIMENTAL

All the chemicals used were of analytical grade purity. Catechol (CAT) and 3,5-di-*tert*-butylcatechol

(DTBC) (Merck and Aldrich Chem. Co. Ltd., respectively) were used as purchased. A zeolite encapsulated copper complex of *o*-phenylenediamine (YCu(OPD)₂) was synthesized and characterized in our laboratory. A neat copper complex of *o*-phenylenediamine (Cu(OPD)₂) was prepared and purified according to the literature procedure [9, 10]. A 30% w/v solution of H₂O₂ (Merck) was used for the preparation of stock solution. The latter was estimated permanganometrically. 1.0×10^{-2} mol/dm³ solutions of substrates were prepared afresh before each set of kinetic runs. All the kinetic runs were carried out at 30°C in phosphate buffers, maintaining H₂O₂ concentration at least ten times greater than that of the substrate. The dielectric constant of the reaction mixtures was varied using methanol. The total dielectric constant ϵ of the reaction mixtures was estimated using the formula $\epsilon = (\epsilon_1 V_1 + \epsilon_2 V_2)/(V_1 + V_2)$, where ϵ_1 and ϵ_2 are the individual dielectric constants of water and methanol, respectively, and V_1 and V_2 are their respective volumes in the reaction mixture. The reaction was initiated with the catalyst, and the progress of the reaction was monitored spectrophotometrically (Shimadzu UV-Vis.160A, Japan) by following the absorbance of the respective products. The molar absorption coefficients of the products were determined using Beer–Lambert's method. In the YCu(OPD)₂ catalyzed reactions, the reaction was monitored simultaneously at two different wavelengths. At one wavelength, the product of the reaction absorbs. At the second wavelength, the product does

¹ This article was submitted by the authors in English.

Table 1. Effect of [substrate], [H₂O₂], and [YC_u(OPD)₂] on the initial rate of reaction I. pH = 5.0; methanol : water = 1 : 9

[catechol] × 10 ³ , mol/dm ³	[H ₂ O ₂] × 10 ² , mol/dm ³	[YC _u (OPD) ₂] × 10 ⁵ , mol/dm ³	Initial rate × 10 ⁷ , mol/(dm ³ s)	k* × 10 ² , dm ⁶ /(mol ² s)
0.3	1.0	2.9	0.1	1.5
0.7	1.0	2.9	0.2	1.1
1.0	1.0	2.9	0.3	1.2
1.5	1.0	2.9	0.6	1.4
1.0	0.5	2.9	0.2	1.3
1.0	2.0	2.9	0.7	1.2
1.0	3.0	2.9	1.0	1.2
1.0	1.0	1.4	0.2	1.3
1.0	1.0	5.7	0.6	1.0
1.0	1.0	8.6	0.9	1.0
1.0	1.0	12.9	1.6	1.3

* Rate constant, k = initial rate/[H₂O₂][sub][catalyst] × 10².

not absorb, and any absorbance detected at this wavelength corresponds to scattering due to the solid catalyst particles. Therefore, the difference between the two absorbance values gives the corrected absorbance of the product. This method is generally employed in atomic absorption spectroscopy [11], and its use in UV-visible spectrophotometry is novel. Its pertinency to the latter is obvious from the good results obtained here. All the kinetic runs were reproducible within an accuracy of ±10% in the catechol reactions and within ±15% in the case of DTBC reactions. The initial rate method was employed to determine the rate of the reaction from the concentration-time data. Initial rates (w_0) were obtained by fitting the data into a polynomial of the form

$$C = a_0 + a_1 t + a_2 t^2 + \dots,$$

where C and t represent concentration and time, respectively, and a_0 , a_1 , a_2 , etc. are constants, and determining the first derivative from the slope of the plot at $t = 0$. Microcal Origin 3.54, Microcal Software Inc, USA, was used for this analysis.

RESULTS

We have studied the kinetics of the following four reactions:

1. Oxidation of catechol by hydrogen peroxide in the presence of YCu(OPD)₂ (reaction I);
2. Oxidation of catechol by hydrogen peroxide in the presence of Cu(OPD)₂ (reaction II);
3. Oxidation of DTBC by hydrogen peroxide in the presence of YCu(OPD)₂ (reaction III); and
4. Oxidation of DTBC by hydrogen peroxide in the presence of Cu(OPD)₂ (reaction IV).

The results of these studies may be summarized as follows. When the kinetic runs were carried out in the presence of varying amounts of substrate ranging from 1×10^{-3} – 1×10^{-2} mol/dm³, the order with respect to the substrate was found to be unity in all the four reactions as indicated by plots of initial rate versus substrate concentration being linear passing through the origin. Similar observation was made for hydrogen peroxide in the concentration range 0.01 to 0.1 mol/dm³, suggesting that the order with respect to [H₂O₂] was also unity for all the reactions. In order to make a comparison of the reaction rates, catalyst variation studies were carried out in such a way that, for both the supported as well as neat catalysts, the metal ion concentration of the catalyst in the reaction mixtures varied in the same range, $(1.4\text{--}14.3) \times 10^{-5}$ mol/dm³. Under this condition, the order with respect to the catalyst was found to be unity in all the cases. The kinetic data obtained during the oxidant, substrate, and catalyst variation studies of the four reactions are given in Tables 1–4, respectively.

Table 2. Effect of [substrate], $[H_2O_2]$, and $[YCu(OPD)_2]$ on the initial rate of reaction II. pH = 6.0; methanol : water = 1 : 9

$[catechol] \times 10^3$, mol/dm ³	$[H_2O_2] \times 10^2$, mol/dm ³	$[YCu(OPD)_2] \times 10^5$, mol/dm ³	Initial rate $\times 10^7$, mol/(dm ³ s)	$k^* \times 10^2$, dm ⁶ /(mol ² s)
0.4	1.0	2.9	2.5	2.1
0.6	1.0	2.9	3.9	2.2
0.8	1.0	2.9	4.8	2.1
1.0	1.0	2.9	5.8	2.0
1.0	0.2	2.9	1.4	2.5
1.0	0.6	2.9	3.6	2.1
1.0	1.0	1.4	3.0	2.1
1.0	1.0	8.6	18.4	2.1
1.0	1.0	10.7	23.6	2.2
1.0	1.0	17.2	37.8	2.2
1.0	1.0	19.3	39.8	2.1

* Rate constant, k = initial rate/ $[H_2O_2][sub][catalyst] \times 10^2$.

Table 3. Effect of [substrate], $[H_2O_2]$, and $[YCu(OPD)_2]$ on the initial rate of reaction III. pH = 5.0; methanol : water = 1 : 9

$[DTBC] \times 10^3$, mol/dm ³	$[H_2O_2] \times 10^2$, mol/dm ³	$[YCu(OPD)_2] \times 10^5$, mol/dm ³	Initial rate $\times 10^7$, mol/(dm ³ s)	$k^* \times 10^2$, dm ⁶ /(mol ² s)
0.2	1.0	2.9	0.5	8.6
0.3	1.0	2.9	0.8	9.1
0.4	1.0	2.9	0.8	7.1
0.5	1.0	2.9	1.1	8.0
0.8	1.0	2.9	1.6	6.9
1.0	1.0	2.9	2.3	8.0
1.0	0.2	2.9	0.5	8.2
1.0	0.6	2.9	1.4	8.3
1.0	0.7	2.9	1.7	8.4
1.0	0.8	2.9	2.0	8.5
1.0	1.0	4.3	3.2	7.4
1.0	1.0	7.2	5.6	7.8
1.0	1.0	10.0	6.7	6.7

* Rate constant, k = initial rate/ $[H_2O_2][sub][catalyst] \times 10^2$.

Table 4. Effect of [substrate], $[H_2O_2]$, and $[YCu(OPD)_2]$ on the initial rate of reaction IV. pH = 5.0; methanol : water = 1 : 9

$[DTBC] \times 10^3$, mol/dm ³	$[H_2O_2] \times 10^2$, mol/dm ³	$[YCu(OPD)_2] \times 10^5$, mol/dm ³	Initial rate $\times 10^7$, mol/(dm ³ s)	$k^* \times 10^2$, dm ⁶ /(mol ² s)
0.2	1.0	2.9	5.5	9.4
0.4	1.0	2.9	10	8.6
0.6	1.0	2.9	12	7.2
0.8	1.0	2.9	18	7.8
1.0	1.0	2.9	25	8.6
1.0	0.2	2.9	5.3	9.1
1.0	0.4	2.9	11	9.4
1.0	0.8	2.9	21	9.1
1.0	0.5	2.9	22	7.9
1.0	0.5	7.1	29	8.3
1.0	0.5	8.4	32	7.7

* Rate constant, k = initial rate/ $[H_2O_2][sub][catalyst] \times 10^2$.

The influence of dielectric constant of the solvent on the reaction rate was studied and it was found that, when the dielectric constant of the medium is increased, the initial rate remains constant for reaction I, increases for reaction III, and decreases for reactions II and IV (Table 5). Correspondingly, a plot of $\log(w_0)$ versus $1/\epsilon$ is a straight line with a positive slope for reactions II and IV and a negative slope for reaction III. Thus, it may be concluded that the active species are oppositely charged in the case of reactions II and IV and are of the

Table 5. Effect of solvent polarity on the initial rate. [Substrate] = 1.0×10^{-3} mol/dm³; [oxidant] = 1.0×10^{-2} mol/dm³; [catalyst] = 2.86×10^{-5} mol/dm³; pH = 5.0 for reaction III and 6.0 for reactions II and IV

Dielectric constant ϵ	Initial rate $\times 10^7$, mol/(dm ³ s)		
	reaction II	reaction III	reaction IV
76.92	5.8	2.3	12.0
71.43	—	1.8	15.6
66.67	8.4	1.5	21.3
62.50	9.9	1.3	26.8

same charge for reaction III. One of the reactive species of reaction I is likely to be neutral.

The results obtained during the pH variation studies are shown in Table 6 from which it is evident that the reactions exhibit a complex dependence on pH.

DISCUSSION

In view of the first order with respect to substrate, catalyst as well as hydrogen peroxide, we assume that the oxidation of DTBC as well as catechol proceeds through the following mechanism: the substrate is oxidized by copper metal ion (Cu^{2+}) in the catalyst, which is thereby reduced to the Cu^+ state. Hydrogen peroxide converts the Cu^+ species back to the Cu^{2+} state.

As can be seen from Table 6, reaction IV exhibits a more or less single pH dependence from pH 6.0 to 8.0. A plot of $1/(initial\ rate)$ versus acid concentration was found to be linear for this reaction (Fig. 1), which can be explained in terms of a rate equation of the form

$$w_0 = \frac{a_4[H_2O_2]_0[DTBC]_0[Cu^{II}(OPD)_2]_0}{b_4 + c_4[H^+]}. \quad (1)$$

The denominator of this equation indicates that the acid dissociation constant of either DTBC or the catalyst is very large and the ratio b_4/c_4 corresponds to the acid dissociation constant of the other.

For reaction III, we propose the rate equation shown below:

$$w_0 = \frac{(a_3 + b_3[H^+])(c_3 + d_3[H^+])[H_2O_2]_0[DTBC]_0[YCu^{II}(OPD)_2]_0}{e_3 + f_3[H^+]}, \quad (2)$$

in which, at low $[H^+]$, $a_3 \gg b_3[H^+]$ and $c_3 \gg d_3[H^+]$ and, at high $[H^+]$ $e_3 \ll f_3[H^+]$ and a_3c_3 is negligible in the numerator. This results in a straight line plot of $1/(initial\ rate)$ versus acid concentration in the pH range 7.0–8.0 (Fig. 2a). By comparing Eqs. (1) and (2), it is easily understood that the term in the denominator of Eq. (2) arises due to the acid dissociation of $YCu(OPD)_2$ and the ratio e_3/f_3 corresponds to the acid dissociation constant, K_2 of $YCu(OPD)_2$. The experimentally determined value for the same was $(2.88 \pm 0.04) \times 10^{-8}$ mol/dm³ (Fig. 2a). Further, a plot of (initial rate) against $[H^+]$ was found to be linear with an intercept at high $[H^+]$, i.e., pH 5.0–6.5 (Fig. 2b) supporting the proposed rate equation. It is also evident from Eqs. (1) and (2) that K_4 , the acid dissociation constant of DTBC, has a magnitude much greater than 10^{-6} . The denominator of Eq. (1) arises due to the acid dissociation of $Cu(OPD)_2$. The value of K_3 , the acid dissociation constant of $Cu(OPD)_2$, was determined from the ratio of the slope

to the intercept of the plot of $1/(initial\ rate)$ against $[H^+]$ for this reaction (Fig. 1) to be $(2.2 \pm 0.2) \times 10^{-7}$ dm³/mol.

For reaction I, we have assumed a rate equation of the form

$$w_0 = \frac{(a_1 + b_1[H^+])[H_2O_2]_0[CAT]_0[YCu^{II}(OPD)_2]_0}{(c_1 + d_1[H^+])(e_1 + f_1[H^+])}, \quad (3)$$

where $c_1 \gg d_1[H^+]$ at low $[H^+]$ and $a_1 \ll b_1[H^+]$ and $e_1 \ll f_1[H^+]$ at high $[H^+]$. The term e_1/f_1 in this case corresponds to the acid dissociation constant of $YCu(OPD)_2$ and is equal to the K_2 obtained from Eq. (2). For the reaction I, a plot of $(initial\ rate)(K_2 + [H^+])$ against $[H^+]$ was found to be linear with an intercept in the pH range 7.0–8.0 (Fig. 3a), supporting the proposed rate equation

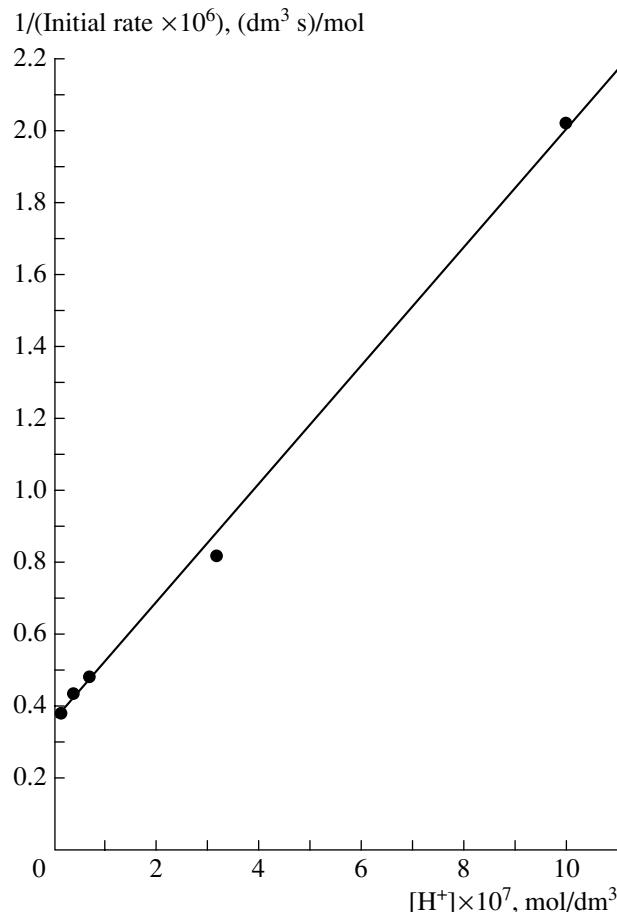


Fig. 1. Effect of pH on the rate of reaction IV.

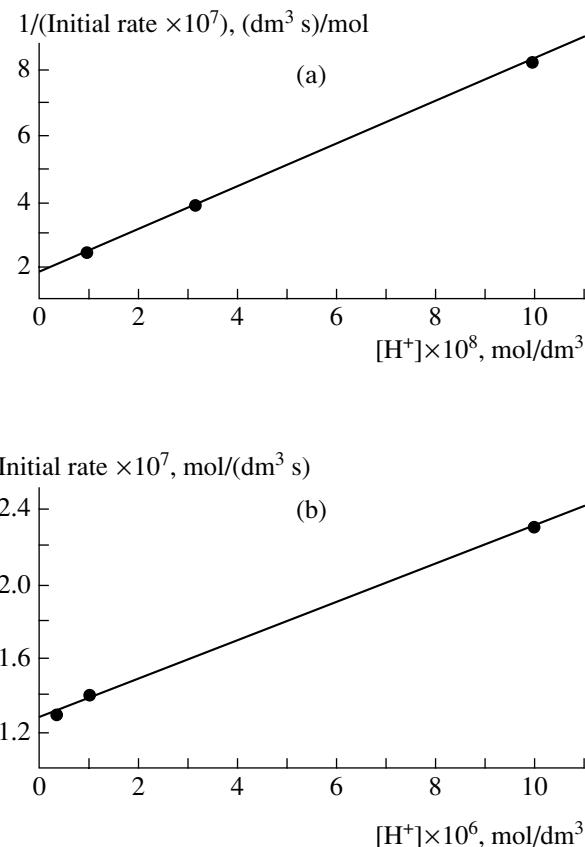


Fig. 2. Effect of pH on the rate of reaction III.

Table 6. Effect of pH on the reaction rates. [Substrate] = 1.0×10^{-3} mol/dm³; [oxidant] = 1.0×10^{-2} mol/dm³; [catalyst] = 2.86×10^{-5} mol/dm³; methanol : water = 1 : 9

Reaction	pH	Initial rate $\times 10^7$, mol/(dm ³ s)	Remarks
I	5.0	0.33	In the pH range 5–6.5, plot of 1/initial rate versus [H ⁺] is linear with intercept (Fig. 3b). In the pH range 7–8, pH dependence is complex
	6.0	1.3	
	6.5	2.1	
	7.0	1.7	
	7.5	1.5	
	8.0	1.3	
II	6.0	4.5	pH dependence is complex throughout
	6.2	5.8	
	6.5	8.1	
	7.0	7.7	
	7.5	5.1	
	8.0	3.9	
III	5.0	2.3	In the pH range 5–6.5, plot of initial rate versus [H ⁺] is linear with intercept (Fig. 2b). In the pH range 7–8, plot of 1/initial rate versus [H ⁺] is linear with intercept (Fig. 2a)
	6.0	1.4	
	6.5	1.3	
	7.0	1.2	
	7.5	2.6	
	8.0	4.1	
IV	6.0	5.0	From pH 6.0–8.0, plot of 1/initial rate versus [H ⁺] is linear with intercept (Fig. 1)
	6.5	12	
	7.2	21	
	7.5	23	
	8.0	26	

and the acid dissociation constant of $\text{YCu}(\text{OPD})_2$ obtained from reaction III. Further, from the plot of 1/(initial rate) versus [H⁺] obtained for reaction I in the pH range 5.0–6.5 (Fig. 3b), the value of K_1 , the acid dissociation constant of catechol, was obtained as $(1.7 \pm 0.3) \times 10^{-6}$ mol/dm³, which corresponds to a pK_a value of 5.77. The most commonly reported value for the pK_a of aqueous catechol is about 9.45 [12–14]. However, recently, Arifien *et al.* studied the pH dependence of absorption spectra of catechol in aqueous solutions and reported a value of 7.15 for the pK_1 of catechol [15]. The value we have obtained is lower than even this value. It is well known that the acid dissociation

constant of phenols is altered by substitution [16]. The pK_a value of catechol obtained in the present study can therefore be explained assuming an intermediate complex formation between catechol and the copper ions in the catalyst. Although no experimental evidence exists for an increase in the acidity of catechol in the presence of metal ions, Zheng and Bruice predicted, through their theoretical calculations, such an increase in acid dissociation of catechol in the presence of magnesium ions with incomplete coordination sphere [17].

The pH dependence observed for reaction II is consistent with the rate equation

$$w_0 = \frac{(a_2 + b_2[\text{H}^+])(c_2 + d_2[\text{H}^+])[\text{H}_2\text{O}_2]_0[\text{CAT}]_0[\text{Cu}^{\text{II}}(\text{OPD})_2]_0}{(e_2 + f_2[\text{H}^+])(g_2 + h_2[\text{H}^+])}, \quad (4)$$

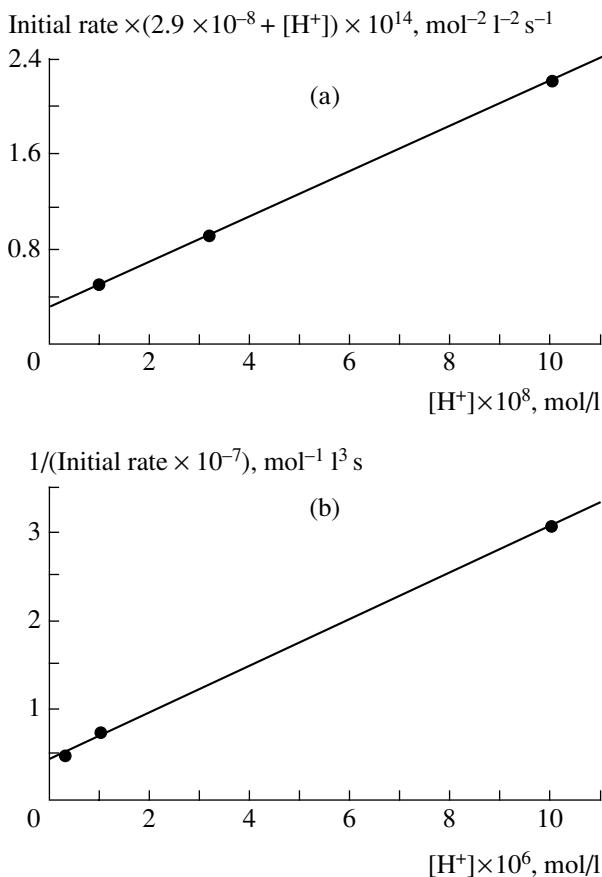


Fig. 3. Effect of pH on the rate of reaction I.

where, at low $[H^+]$ $e_2 \gg f_2[H^+]$ and $c_2 \gg d_2[H^+]$ and, at high $[H^+]$, $\{e_2 + f_2/[H^+]\} \sim (a_2 + b_2[H^+])$. The terms $\{e_2 + f_2[H^+]\}$ and $\{g_2 + h_2[H^+]\}$ arise due to the acid dissociation of catechol and $\text{Cu}(\text{OPD})_2$, respectively. For this reaction, a plot of (initial rate)($w_0 (K_3 + [H^+])$ versus $[H^+]$ was linear in the pH range 7.0–8.0 (Fig. 4a), supporting the proposed rate equation and the acid dissociation constant of $\text{Cu}(\text{OPD})_2$ obtained from reaction IV. As may be expected from the rate equation, a similar plot was obtained in the pH range 6.0–6.5 with a different slope (Fig. 4b).

When the effect of dielectric constant on the reaction rates is considered, it may be seen that, in reaction I, one of the reactants is nonpolar. From the dielectric and pH effects observed for this reaction, it is not possible to decide whether the neutral species is that of catechol or the catalyst. However, we assume the neutral species to be that of the catalyst since it is reduced during the reaction. In reaction II, one of the reactants is positive and the other is negative. It is obvious that both protonated and unprotonated $\text{Cu}(\text{OPD})_2$ are positive species. Therefore, the negative reactive species is that of catechol. This indicates that the unprotonated reactive species is that of catechol and is the predominant reactive species at pH 6.2 where the dielectric effect was stud-

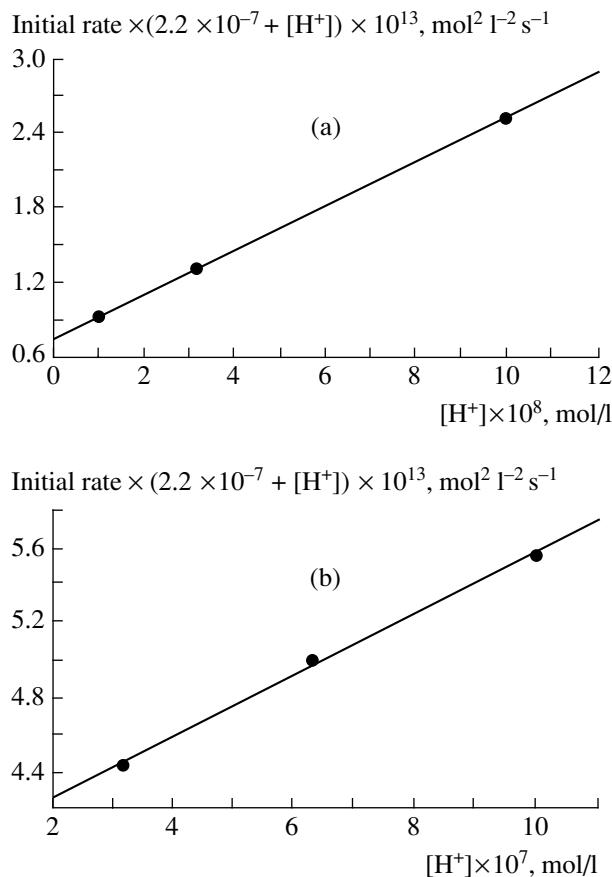


Fig. 4. Effect of pH on the rate of reaction II.

ied. In reaction III, the dielectric effect indicates that both the reactive species of DTBC and $\text{YC}(\text{OPD})_2$ are negatively charged at pH 5.0. This indicates that one of the species of $\text{YC}(\text{OPD})_2$ is negatively charged. We assume this species to be the unprotonated one and the protonated one to be neutral. In reaction IV again, the dielectric effect indicates one of the reactive species is positively charged while the other is negatively charged. Since in this case both the reactive species are unprotonated, this further confirms that unprotonated $\text{Cu}(\text{OPD})_2$ is positively charged.

Although the pH and dielectric effects indicated that the four reactions involve different reactive species, the orders with respect to substrate, hydrogen peroxide, and the catalyst were unity in all the four reactions suggesting that the mechanism of all these reactions is the same. Since the reaction is third-ordered, we assume the formation of copper(I) intermediate from the catalyst by interaction with the substrate, which is subsequently oxidized by hydrogen peroxide. Thus, the mechanism of the reactions I–IV includes equilibrium deprotonation stages for the substrates and catalysts, reduction stages of different forms of the catalysts by different forms of the substrates, and the oxidation of the reduced form of the catalyst by hydrogen peroxide.

CONCLUSIONS

The present study indicated that the mechanism of oxidation of catechol and DTBC by hydrogen peroxide is not altered by the change in the coordination sphere around the metal ion due to encapsulation. However, the catalysis by zeolite encapsulated complex was slower than that by the neat complex. The slowing down of the reaction in the zeolite case is probably due to the constraint imposed by the zeolite framework. The rate of DTBC oxidation was found to be greater than the rate of catechol oxidation. This is obviously due to the electron donating tertiary butyl groups present in the benzene ring.

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