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Study on phenol oxidation with H_2O_2 catalyzed by Schiff base manganese complexes as mimetic peroxidase

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Abstract: Two new ligands, 1-hydroxy-5-[4-(2-hydroxybenzylideneamino)phenoxy]-3-oxapentane (HL^1) and 1-methoxy-5-[4-(2-hydroxybenzylideneamino)phenoxy]-3-oxapentane (HL^2), and their Mn(III) complexes were synthesized and characterized. The two new Schiff base Mn(III) complexes were used to mimic peroxidase in the oxidation of phenol by hydrogen peroxide. The effect of the mole ratio of H_2O_2 to the complex, pH and temperature on the reaction rate was investigated. The mechanism of the catalytic oxidation is discussed. A kinetic mathematic model for the oxidation of phenol catalyzed by Schiff base Mn(III) complexes has been constructed.

Keywords: Schiff base manganese complexes, phenol catalytic oxidation, kinetics.

INTRODUCTION

Since the 1980's, the oxidation of phenol catalyzed by mimic peroxidase with H_2O_2 has received considerable attention.[1–3] The study of the oxidation of phenol catalyzed by peroxidase mimics is significantly important for not only could it provide useful information for the elucidation of the reaction mechanism but also be applied in analytical clinical chemistry, in the synthesis of phenolic polymers and in the protection of the environment.[4–7]

The synthesis and application of Schiff base complexes containing a transition metal ion have been highly considered in inorganic, organic and biological fields,[8] because their structures are similar to the porphyrin ring and phthalocyanine ring, and they are good at loading oxygen, resisting bacteria and mimicking enzymes.[9] Previous studies[10,11] indicate that some Schiff base transition metal complexes have high catalytic activity as natural oxidases, and some Schiff base complexes

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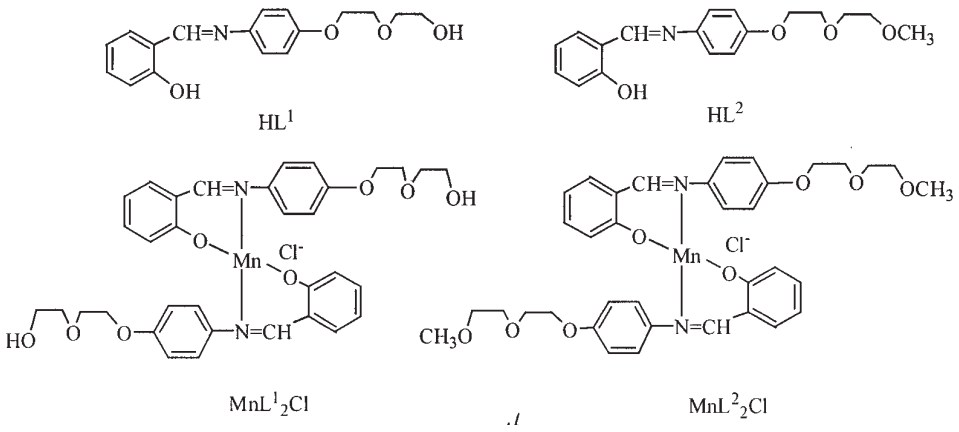


Fig. 1. The structures of the ligands and complexes.

can be used in the catalytic oxidation of phenol as peroxidases. In previous studies, simple Schiff base complexes were used as peroxidases for the catalytic oxidation of phenol.[12–14] In order to develop new catalysts and study further the mechanism and kinetics of the catalytic oxidation of phenols, two new Schiff base Mn(III) complexes ($MnL^1{}_2Cl$, $MnL^2{}_2Cl$) bearing polyether side chains were synthesized, characterized, and used for the catalytic oxidation of phenol (See Fig. 1).

EXPERIMENTAL

Materials

Two ligands, 1-hydroxy-5-(4-aminophenoxy)-3-oxapentane and 1-methoxy-5-(4-aminophenoxy)-3-oxapentane, were supplied by Sichuan University Organic Chemistry Institute. Deionized water was used for the kinetic study. Phosphate buffer solutions, the ionic strength of which were maintained at 0.1 mol dm^{-3} with potassium nitrate, were used. The phenol was purchased from Shanghai Chemical Co. Ltd. The phenol stock solution for the kinetic study was prepared using redistilled H_2O. Silica gel was used for column chromatography. All reagents were of analytical grade and were used without further purification.

Apparatus and instrumentation

Melting points were determined on a Yanaco MP-500 micro-melting point apparatus and are uncorrected. The infrared spectra were recorded on a Nicolet-1705X spectrometer. The ^{1}H-NMR spectra were recorded on a Bruker AC-200 MHz spectrometer using tetramethylsilane as internal standard. The mass spectra were obtained on a Finnigan MAT 4510 spectrometer and a Finnigan LCQ^{-DECA} spectrometer. The manganese content was measured by an IRIS-Advantage ICP emission spectrometer. Other elementary analyses were performed on a Carlo Erba 1106 elemental analyzer. The molar conductance was obtained on a DDS-11A conductimeter. The kinetic studies were performed by UV-Vis methods with a GBC 916 UV-Vis spectrophotometer equipped with a thermostatic cell holder. High-pressure liquid chromatography (HPLC) was performed on a Varian 2000 chromatograph with a Hypersil ODS column (25 cm × 5 μm), with UV-Vis spectrophotometric detection.

Syntheses and characterization

1-Hydroxy-5-[4-(2-hydroxybenzylideneamino)phenoxy]-3-oxapentane ligand (HL^1). 1-Hydroxy-5-(4-aminophenoxy)-3-oxapentane (1.97 g, 10.0 mmol), ethanol (10 cm^3), and salicylaldehyde

(1.22 g, 10.0 mmol) were stirred under N_2 atmosphere for 2 h, then the volume of the mixture was reduced to an appropriate level and the mixture was chromatographed (stationary phase: silica gel 60H, eluent: CH_3COOEt) to give a yellow oil, 2.41 g, 81 % yield. ^{1}H-NMR [deuterium substituted chloroform ($CDCl_3$) was used as solvent], chemical shift (δ): 13.52 ppm [*s*, 1H, OH, D_2O exchange (single peak, attributed to the hydrogen of the "OH")]; 8.40 ppm [*s*, 1H, CH=N (single peak, attributed to the hydrogen of "CH=N")], 7.40–7.10 ppm [*m*, 4H, Ar–H (multi-peak, attributed to the four hydrogens of "Ar–H")], 7.00–6.90 ppm [*m*, 4H, Ar–H (multi-peak, attributed to the four hydrogens of "Ar–H")], 4.14–3.87 ppm [*m*, 8H, OCH_2CH_2O (multi-peak, attributed to the eight hydrogens of the two "OCH_2CH_2O")], 3.30 ppm (*s*, 1H, OH, D_2O exchange); IR [neat (liquid film method)] ν_{max}: 3458, 3220, 1622, 1235, 1130 cm^{-1}; MS *m*/*z* (mass spectrum ratio of mass to charge): 301 [M^+ (ion peak)]. Anal. Calcd. (calculated values) for $C_{17}H_{19}NO_4$: C 67.77, H 6.31, N 4.65; found (experimental values) C 67.55, H 6.56, N, 4.81.

1-Methoxy-5-[4-(2-hydroxybenzylideneamino)phenoxy]-3-oxapentane ligand (HL^2). HL^2 was prepared as described for HL^1 to obtain a yellow oil, 2.46 g, 78 % yield. ^{1}H-NMR ($CDCl_3$) δ: 13.51 (*s*, 1H, OH, D_2O exchange), 8.60 (*s*, 1H, CH=N), 7.36–7.10 (*m*, 4H, Ar–H), 7.00–6.94 (*m*, 4H, Ar–H), 4.18–3.86 (*m*, 8H, OCH_2CH_2O), 3.72 (*s*, 3H, OCH_3); IR (neat) ν_{max}: 3210, 1618, 1235, 1138 cm^{-1}; MS *m*/*z*: 315 (M^+). Anal. Calcd. for $C_{18}H_{21}NO_4$: C 68.57, H 6.67, N 4.44; found C 68.71, H 6.49, N 4.69.

General methods for the preparation of the complexes ($MnL^1{}_2Cl$ and $MnL^2{}_2Cl$). A solution of the ligand (HL^1 or HL^2) (1.0 mmol) and $MnCl_2{\cdot}4H_2O$ (1.1 mmol) in EtOH (15 cm^3) was stirred for 2 h under a N_2 atmosphere at 70 ºC, then the mixture was cooled, filtered and washed with EtOH to give the complexes. The pure product was obtained after recrystallization from EtOH.

$MnL^1{}_2Cl$: purple, 71 % yield. m.p.: 256–260 ºC. IR (KBr, film) ν_{max}: 3510, 1636, 1230, 1126 cm^{-1}. MS *m*/*z*: 692 ($M^+ + 1$). Anal. Calcd. for $MnC_{34}H_{36}N_2O_8Cl$: C 59.04, H 4.49, N 4.05, Mn 7.97; found C 58.79, H 4.63, N 3.88, Mn 7.68. Λ_m = 101.3 S cm^2 mol^{-1}.

$MnL^2{}_2Cl$, purple, 65 % yield. m.p: > 300 ºC. IR (KBr, film) ν_{max} 1636, 1228, 1135 cm^{-1}. MS *m*/*z*: 719 (M^+). Anal. Calcd. for $MnC_{36}H_{40}N_2O_8Cl$: C 60.09, H 5.56, N 3.89, Mn 7.65; found C 59.88, H 5.73, N, 4.01, Mn 7.88. Λ_m = 98.6 S cm^2 mol^{-1}.

The elemental analysis of the complexes indicates that the ligand to manganese ion ratio is 2:1 (ligand / metal) for the studied Schiff base complexes. Moreover, the observed molar conductance of all the complexes in DMF solution (1.0×10^{-5} mol dm^{-3}) at 25 ºC also show they are electrolytes[15] with manganese in its trivalent form. The IR spectra of the complexes show that the IR absorbance is still in the same frequency range except the C=N stretches which were shifted slightly (14–18 cm^{-1}) to higher frequencies and the OH stretches (3210–3220 cm^{-1}) which were absent after the formation of the complexes.

Kinetics method

Each kinetic run was initiated by injecting an aqueous solution of phenol of a given concentration into a 1 cm cuvette containing 3 mL buffer solution. The solution was composed of a Schiff base complex and H_2O_2 of the desired concentrations. The rate for the change of the phenol concentration in the buffer solution was determined by monitoring the decrease of the absorbancy (*A*) at 270 nm. The phenol was added in a 10-fold excess over the concentration of the complex. The apparent first order rate constants (k_{ob}) of the oxidation of phenol were obtained using the initial rate method.[14] The ionic strength of all reactions was 0.1 mol dm^{-3}.

Analysis of the reaction products

The catalytic oxidation of phenol was completed at pH 7.0, 25 ºC, $[MnL_2] = 3 \times 10^{-5}$ mol dm^{-3}, $[H_2O_2] = 1 \times 10^{-3}$ mol dm^{-3}, $[S]_0 = 5.0 \times 10^{-4}$ mol dm^{-3}, where $[S]_0$ is the initial concentration of the substrate phenol. After the kinetic run, the mixture for the catalytic oxidation of phenol was left for a total of 8 h, and then analyzed by HPLC. Catechol and hydroquinone were identified in the reacted solution by comparison with authentic specimens.

RESULTS AND DISCUSSION

Rate of catalytic oxidation of phenol

The apparent first order rate constants (k_{ob}) in Table I were obtained by varying the pH of the solution for each concentration of phenol with a given concentration of the Schiff base complex. Synchronously, the apparent first order rate constants (k_0) of phenol oxidation using only H_2O_2 as the oxidant was 1.2×10^{-5} s^{-1}, as obtained according to the initial rate method at pH 7.0, [phenol] = 3×10^{-4} mol dm^{-3}, and [H_2O_2] = 1×10^{-3} mol dm^{-3}.

TABLE I. The effect of pH and the concentration of phenol on k_{ob} (s^{-1})

10^4 [S]$_0$ mol dm^{-3}	10^2 k_{ob} ($MnL^1{}_2Cl$)/s^{-1}					10^2 k_{ob} ($MnL^2{}_2Cl$)/s^{-1}				
	pH					pH				
	8.5	8.0	7.0	6.0	5.5	8.5	8.0	7.0	6.0	5.5
3.0	2.36	3.25	5.37	4.37	3.68	2.34	3.23	3.62	2.91	2.64
4.0	2.97	4.13	7.56	5.34	4.56	3.05	4.01	4.57	3.86	3.24
5.0	3.52	4.98	8.76	6.32	5.37	3.56	4.81	5.51	4.51	4.06
6.0	4.36	5.75	9.58	7.64	6.52	4.07	5.63	6.43	5.26	4.74
7.0	4.88	6.58	10.33	8.37	7.06	4.64	6.27	7.34	6.07	5.12
8.0	5.23	7.52	12.36	9.27	7.89	5.04	7.02	8.12	6.34	5.87

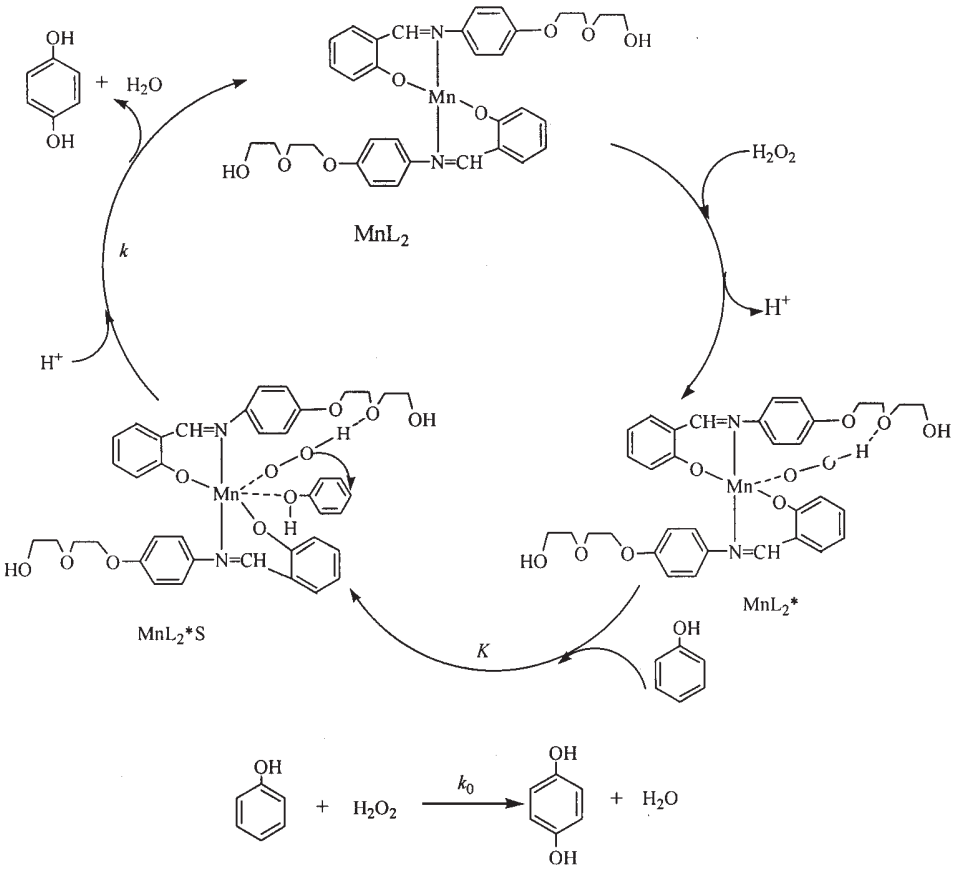
Reaction conditions: T = 25 ºC, [MnL_2] = 3×10^{-5} mol dm^{-3}, [H_2O_2] = 1×10^{-3} mol dm^{-3}

Comparison of k_0 with k_{ob} in Table I shows that the reaction rate for the catalytic oxidation of phenol increased by a factor of *ca.* 4.5×10^3 for the complex $MnL^1{}_2Cl$, and by a factor of *ca.* 3×10^3 for the complex $MnL^2{}_2Cl$ at pH 7.0, [phenol] = 3.0×10^{-4} mol dm^{-3}. These results show that the two Schiff base complexes are good catalysts for the catalytic oxidation of phenol.

Reaction mechanism of the catalytic oxidation of phenol

The Schiff base complexes used in the experiment are similar to metal-porphyrins complexes and metal-phthalocyanines in terms of structures[16] and analysis of the spectral characteristics shows that an active species MnL_2* may be generated in the H_2O_2–buffer solution. Hence, the process of phenolic oxidation in the MnL_2–H_2O_2 system may be similar to that in the H_2O_2–natural peroxidase system. According to the experimental data above, the proposed process of the catalytic oxidation of phenol in the MnL_2–H_2O_2 system is illustrated in Scheme 1.

Scheme 1 shows that the active species MnL_2^* is first generated quickly in the MnL_2–H_2O_2–buffer solution, then the intermediate MnL_2^*S is generated by coordination of phenol to Mn^{3+} and a rapid pre-equilibrium between MnL_2^* and MnL_2^*S is established with an equilibrium-constant K. The intermediate MnL_2^*S is stabilized by



Scheme 1. The mechanism of the oxidation of phenol catalyzed by the Schiff base complexes.

the formation of hydrogen bond between phenol and the oxygen atom of the polyether side chains of the Schiff base complex. Finally in the rate determining step, the products are obtained and the catalyst is reverted back to MnL_2 with a first order rate constant k. In this process, the intermolecular oxidation-reduction reaction between the substrate phenol and H_2O_2 is transformed into an intramolecular electron transfer reaction in the intermediate $MnL_2{}^*S$, which leads to a large decrease of the activation energy for phenol oxidation and the rate of phenol oxidation is greatly enhanced.

Kinetics of the catalytic oxidation of phenol

According to Scheme 1, the rate equation can be written as:

$$-dc/dt = k[MnL_2{}^*S] \quad (1)$$

where k is the first order rate constant for product formation and $[MnL_2{}^*S]$ is the concentration of the intermediate formed by the substrate and the active species in the buffer solution. The rate constant (k_0) for the oxidation of phenol by H_2O_2 in

the absence of catalyst was not considered in Eq. (1) due to the fact that it is very small compared with the k_{ob} of the catalytic oxidation of phenol.

According to the mass balance, one has:

$$[MnL_2^*] = [MnL_2^*]_t - [MnL_2^*S] \quad (2)$$

where $[MnL_2^*]$ and $[MnL_2^*]_t$ are the free and the total concentration of the active species, respectively.

The association constants K can be expressed in terms of concentrations:

$$K = [MnL_2^*S]/[MnL_2^*][S] \quad (3)$$

where K is the association constant between the substrate and the active species; [S] is the free substrate concentration, which can be substituted by the initial concentration of the substrate based on the initial rate method ($[S] = [S]_0 - [MnL_2^*S]$).

Combination of Eqs. (2) and (3) leads to:

$$[MnL_2^*S] = \frac{[S][MnL_2^*]_t}{\frac{1}{K} + [S]} \quad (4)$$

Combination of Eqs. (1) and (4) gives:

$$-dc/dt = \frac{k[S]}{\frac{1}{K} + [S]}[MnL_2^*]_t = k_{ob}[MnL_2^*]_t \quad (5)$$

where in Eq. (5):

$$k_{ob} = \frac{k[S]}{\frac{1}{K} + [S]} \quad (6)$$

Rearranging Eq. (6) results in:

$$\frac{1}{k_{ob}} = \frac{1}{k} + \frac{1}{Kk[S]} \quad (7)$$

In accordance with Eq. (7) straight lines for $1/k_{ob}$ *versus* 1/[S] were obtained using the data given in Table I (Fig. 2), indicating that the proposed mechanism is reasonable. On the basis of Fig.2, the value of k for the catalytic oxidation of phenol in different buffer solutions were determined from the results of the linear fit by the least-square method and are shown in Table II.

TABLE II. The values of k (s^{-1}) obtained for the oxidation of phenol catalyzed by MnL_2

Complex	k/s^{-1}				
	pH 8.5	8.0	7.0	6.0	5.5
$MnL^1{}_2Cl$	0.22	0.30	0.43	0.28	0.25
$MnL^2{}_2Cl$	0.16	0.23	0.31	0.25	0.21

Reaction conditions: T = 25 ºC, $[MnL_2] = 3 \times 10^{-5}$ mol dm^{-3}, $[H_2O_2] = 1 \times 10^{-3}$ mol dm^{-3}

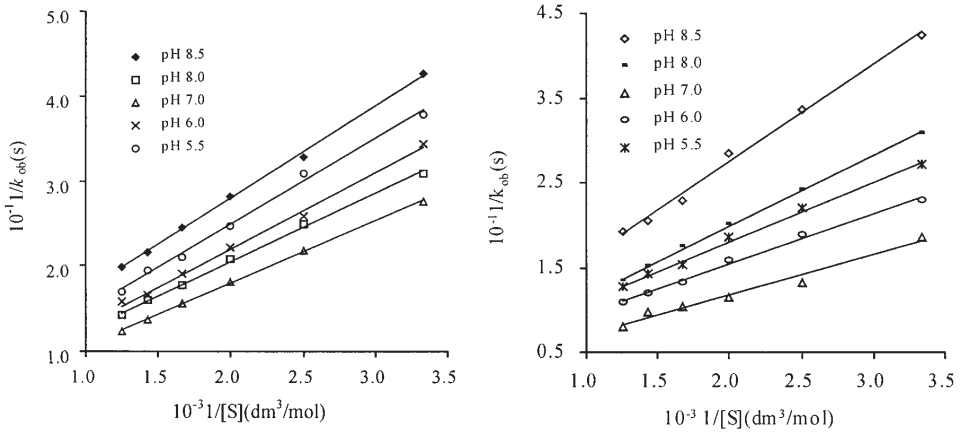


Fig. 2. The determination of k from the plots of $1/k_{ob}$ *versus* 1/[S]. Reaction conditions: T = 25 ºC, $[MnL_2] = 3 \times 10^{-5}$ mol dm^{-3}, $[H_2O_2] = 1 \times 10^{-3}$ mol dm^{-3}.

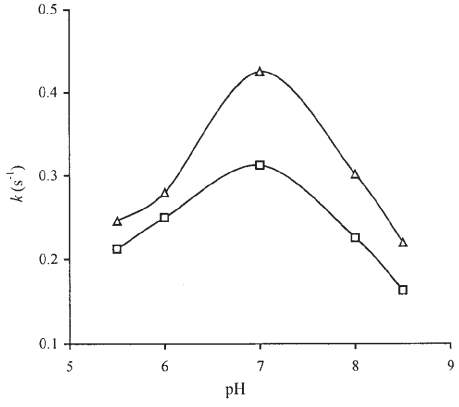


Fig. 3. The effect of pH on the rate of the reaction for both catalysts (Δ: $MnL_2{}^1Cl$; □:$MnL_2{}^2Cl$). Reaction conditions: T = 25 ºC, [S] = 3×10^{-4} mol dm^{-3}, $[MnL_2] = 3 \times 10^{-5}$ mol dm^{-3}, $[H_2O_2] = 1 \times 10^{-3}$ mol dm^{-3}.

Optimum acidity for the catalytic oxidation of phenol

The acidity of the reaction system is an important factor in controlling the rate of the enzymatic catalyzed oxidation of phenol,[17] because the ionic state on the surface of the peroxidase is controlled by the acidity of the reaction system and, hence, the spatial conformation of the enzyme is transformed and the enzymatic activity is changed depending on the acidity of the reaction system. Moreover, the stability of the intermediate ($MnL_2{}^*S$) formed from the substrate and the active species would also be changed with chaining acidity of the reaction system. Therefore, the rate of the catalytic reaction is controlled by the acidity of the reaction system, which must be strictly controlled in the enzymatic catalytic reaction. The performances of the mimic peroxidase in the present study are similar to that of the natural enzyme. Figure 3 shows that the first order rate constant (k) of the catalytic oxidation of phenol is correlated to the acidity of the reaction medium in the H_2O_2–MnL_2–buffer solution system. The k of the catalytic oxidation of phenol initially increases, up to a maximum, and then falls when the pH value of solution is increased from 5.5 to 8.5, which is similar to the rate change following the change of the solution acidity in the oxidation of phenol catalyzed by natural peroxidase. The optimum acidity of the enzyme-like system in the present study was *ca.* pH 7.0, while the optimum value for catalysis by horseradish peroxidase was *ca.* pH 5.8 in phosphate buffer.[1]

In the reaction mechanism shown in Scheme 1, the step from $MnL_2{}^*S \rightarrow MnL_2 + P$ may contain the step $MnL_2{}^*S \rightleftharpoons MnL_2{}^*S^- + H^+$, *i.e.*, the intermediate $MnL_2{}^*S$ is first ionized, then the products are formed due to electron transfer inside the intermediate $MnL_2{}^*S^-$. The rate of phenol oxidation depends on the stability of the intermediate $MnL_2{}^*S^-$. According to the principles of chemical equilibria, acidic conditions are unfavorable for the formation of the intermediate $MnL_2{}^*S^-$ and, hence, for the generation of the products from the intermediate $MnL_2{}^*S$. In addition, the reaction $MnL_2{}^* + OH^- \rightarrow MnL_2{}^*OH^-$, which is a competing or unrelated side reaction, would be favoured under alkaline conditions, which are, therefore, also unfavorable for the formation and stabilization of the intermediate $MnL_2{}^*S^-$ as well as for the reformation of the catalyst MnL_2. Hence, the first order rate constants (k) increase with increasing pH up to pH 7, but decrease with further increasing of the pH.

Selection of the optimum mole ratio of H_2O_2/catalyst in the reaction system

The experimentally determined apparent first order rate constants of the catalytic oxidation of phenol changed with varying mole ratios of H_2O_2 to complex, which is illustrated in Fig. 4. Thus, the apparent first order rate constants of the catalytic oxidation of phenol in the system H_2O_2–MnL_2–buffer solution initially increase, up to a maximum, and then fall when the mole ratio of H_2O_2 to complex was increased from 0 to 80; the optimum mole ratio of H_2O_2 to complex is about 30. These results are similar to those of Maloney[18] on the removal of organic chemicals catalyzed by horseradish peroxidase.

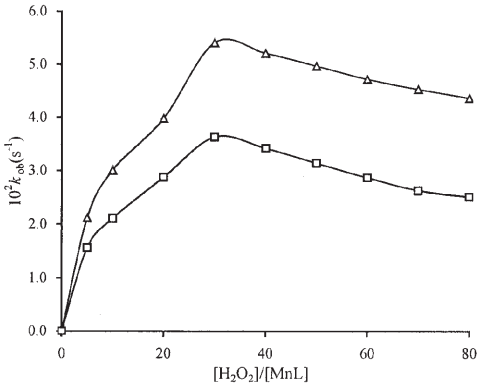


Fig. 4. The effect of $[H_2O_2]/[MnL_2]$ on the apparent first order rate constant k_{ob} (s^{-1}) (Δ: MnL_2^1 Cl; □:MnL_2^2 Cl). Reaction conditions: pH = 7.0, [S] = 3×10^{-4} mol dm^{-3}, $[MnL_2] = 3 \times 10^{-5}$ mol dm^{-3}

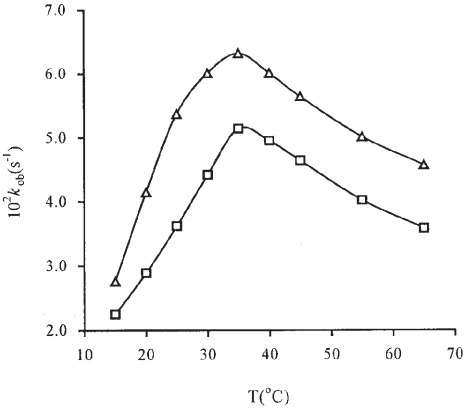


Fig. 5. The effect of temperature on the apparent first order rate constant k_{ob} (s^{-1}) (Δ: MnL_2^1 Cl; □:MnL_2^2 Cl). Reaction conditions: pH 7.0, [S] = 3×10^{-4} mol dm^{-3}, $[MnL_2] = 3 \times 10^{-5}$ mol dm^{-3}, $[H_2O_2] = 1 \times 10^{-3}$ mol dm^{-3}.

Selection of the optimum temperature for the catalytic reaction

The experiments were conducted at different temperatures in order to investigate the effect of temperature on the rate of catalytic oxidation of phenol in buffer solutions. The results are shown in Fig. 5, from which it can be observed that the apparent first order rate constants of the reaction change in a bell-shaped manner when the medium temperature is changed from 15 ºC to 65 ºC. The optimal temperature was found to be about 35 ºC for both Schiff base complexes, as mimic peroxidases.

Before reaching the optimum temperature, the rate of the formation of the active species MnL_2^* and the intermediate MnL_2^*S should increase with increasing temperature, hence, the rate of phenol oxidation is enhanced with increasing temperature. A further temperature increase leads to a change of the spatial conformation of the Schiff base complexes as mimic enzymes and to the occurrence of unrelated reactions of the H_2O_2 (such as H_2O_2 decomposition), thereby reducing the catalytic efficiency of the mimic enzyme and the effective concentration of H_2O_2.

CONCLUSION

The two Schiff base complexes containing manganese ions demonstrated good catalytic activity and a catalytic character similar to that of a natural enzyme for the catalytic oxidation of phenol. The reaction rate of the oxidation of phenol using H_2O_2 as the oxidant in the complexes–buffer solution increases by a factor of *ca.* $3 \times 10^3 - 4.5 \times 10^3$, compared to that in the absence of a catalyst. The catalytic activity of the Schiff base complexes changes with changing $[H_2O_2]/[MnL_2]$, temperature and pH of the reaction system, which is in accordance with the behaviour of the natural enzyme. The catalysis by the Schiff base complexes can be explained according to the simulative peroxidase model proposed in this paper.

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ИЗВОД

ПРОУЧАВАЊЕ ОКСИДАЦИЈЕ ФЕНОЛА СА H_2O_2 КАТАЛИЗОВАНЕ КОМПЛЕКСИМА МАНГАНА СА ШИФОВИМ БАЗАМА КАО ИМИТАЦИЈАМА ПЕРОКСИДАЗЕ

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Синтетисана су и карактерисана два нова лиганда, 1-хидрокси-5-[4-(2-хидроксибензилиденамино)фенокси]-3-оксапентан (HL^1) и 1-метокси-5-[4-(2-хидроксибензилиденамино)фенокси]-3-оксапентан (HL^2). Комплекси Mn(III) са ове две нове Шифове базе коришћени су да имитирају пероксидазу при оксидацији фенола водоник-пероксидом. Испитивани су утицаји молског односа H_2O_2 са комплексима, pH и температуре на брзину реакције. Дискутован је механизам каталитичке оксидације и направљен кинетички математички модел оксидације фенола катализоване комплексима Шифових база са Mn(III)**.**

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