Oxidation of hydrogen peroxide by [Ni^{III}(cyclam)]$^{3+}$ in aqueous acidic media

SANKARAN ANURADHA and VENKATAPURAM RAMANUJAM VIJAYARAGHAVAN*

Department of Physical Chemistry, University of Madras, Guindy Campus, Chennai 600 025, India
e-mail: smradha73@gmail.com; viju47@yahoo.co.in

Abstract. The kinetics of oxidation of H_2O_2 by [Ni^{III}(cyclam)]$^{3+}$, [Ni^{III}L$_1$], was studied in aqueous acidic media at 25°C and I $= 0.5$ M (NaClO$_4$). The [Ni^{III}L$_1$] to [Ni^{II}L$_1$] reduction was found to be fast in the presence of Cu(II) ion than the oxidation of the cyclam ligand by $^\cdot$OH. The rate constant showed an inverse acid dependence on H$^+$ ion at the pH range 1–1.5. The presence of sulphate retards the reaction. Macrocylic ligand oxidation was followed spectrophotometrically by examining the oxidation of nickel(II) complexes of macrocyclic ligands such as 1,8-bis(2-hydroxyethyl)-1,3,6,8,10,13-hexaazacyclotetradecane (L$_2$), *ms*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (L$_3$), *rac*-Me$_6$[14]-4,11-dieneN$_4$ (L$_4$) by reaction with hydrogen peroxide. The rate constant for the cross reaction is discussed in terms of Marcus relationship.

Keywords. Nickel(III) cyclam; hydrogen peroxide oxidation; Cu(II) catalyst.

1. Introduction

Extensive reports are available in literature on the metal ion-catalysed decomposition of hydrogen peroxide. It has been suggested that the equilibria for the complex formation between hydrogen peroxide and the aqua–cations Fe^{III}(aq),[1–3] Ce^{IV}(aq),[4,5] Mn^{III}(aq),[4,6] Co^{III}(aq),[4,7,8] and Ag^{II}(aq)[4,9] are established more rapidly than the rate of decomposition of hydrogen peroxide. The kinetic study of the complex formation between iron(III)-EDTA with hydrogen peroxide in aqueous solution was carried out in alkaline medium.[10] At higher acidity ([H$^+$] > 0.5 mol dm^{-3}), the kinetics of oxidation of hydrogen peroxide by [Ni(bipy)$_3$]$^{3+}$ was found to be independent of [H$^+$] and no replacement of the ligand on the nickel(III) centre by H_2O_2 was observed.[11] Oxidation of hydrogen peroxide by tris(2,2′-bipyridine) and tris(4,4′-dimethyl-2,2′-bipyridine) complexes of osmium(III), iron(III), ruthenium(III), and nickel(III) studied in acidic and neutral aqueous media, show an inverse acid dependence over the pH the range 6.0–8.5.[12] Kinetic measurements with an excess of H_2O_2 revealed that HO$_2^-$ is the only redox–active species for the reaction with [Ni(tacn)$_2$]$^{3+}$ under conditions 2 < pH < 5.5, while the

participation of both H_2O_2 and HO$_2^-$ was observed for the reactions with [Fe(ttcn)$_2$]$^{3+}$ and [Ru(bipy)$_3$]$^{3+}$. The reaction pathway for the oxidation of hydrogen peroxide in acidic solution by [Ni(tacn)$_2$]$^{3+}$ involves interaction of HO$_2^-$ with the amino hydrogen atom on the tacn ligand.[13]

An attempt for reduction of [Ni^{III}L$_1$] centre by H_2O_2 revealed that it was slow and complicated by the ligand oxidation. Reaction of [NiL$_1$]$^{2+}$ with hydrogen peroxide in acidic media results in the formation of a dimeric complex in which there is an evidence for electron delocalization across the M–M distance.[14] Laurence *et al.*, studied that the nickel(III) complexes of the ligands (L$_3$ and L$_4$) which contain NH groups are converted into nickel(II) complexes of radical forms of the ligands at pH > 3.[15] The pulse radiolysis study suggested that the hydroxyl radicals oxidize the nickel(II) complexes by initial H-atom abstraction from the ligand, and the nickel(III) complexes are then formed by proton-assisted intramolecular electron transfer. Homolytic O–O cleavage for the reaction of [Ni^{II}cyclam(CH$_3$CN)$_2$](ClO$_4$)$_2$ with TBHP (*tert*-Butyl hydroperoxide) in CH$_3$CN and proton assisted heterolysis for O–O activation in H_2O was studied.[16] In this paper, we report kinetics of Cu(II) catalysed oxidation of hydrogen peroxide by [Ni^{III}L$_1$]. Nickel(II) complexes of macrocyclic ligands in scheme 1 were examined towards ligand oxidation by carrying out oxidation of metal centre by hydrogen peroxide and *t*-Butyl hydroperoxide.

_____
*For correspondence
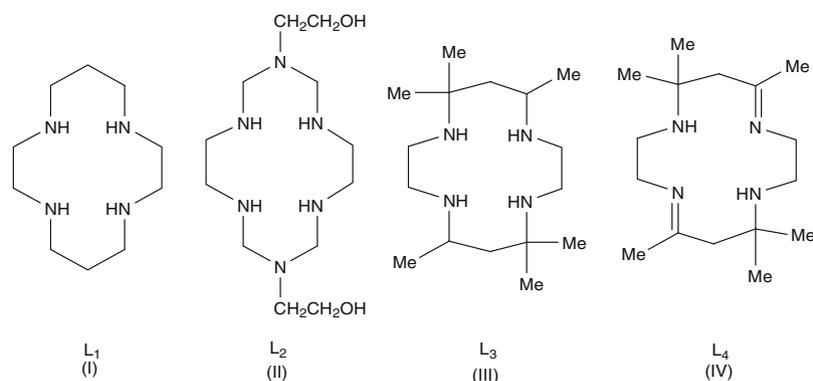
Scheme 1. Structure of macrocyclic ligands.

2. Experimental

2.1 *Materials and reagents*

$[NiL_1](ClO_4)_2$, and the corresponding $[NiL_1(NO_3)_2]ClO_4$ complexes were prepared as described previously.[17,18] $[NiL_2](ClO_4)_2$ ($\varepsilon_{444} = 54$ M^{-1} cm^{-1}, $\varepsilon_{205} = 15,300$ M^{-1} cm^{-1}), $[NiL_3](ClO_4)_2$ ($\varepsilon_{437} = 100$ M^{-1} cm^{-1}, $\varepsilon_{282} = 7,140$ M^{-1} cm^{-1}, $\varepsilon_{215} = 22,000$ M^{-1} cm^{-1}), and $[NiL_4](ClO_4)_2$ ($\varepsilon_{463} = 68$ M^{-1} cm^{-1}, $\varepsilon_{236} = 12,900$ M^{-1} cm^{-1}, $\varepsilon_{207} = 8,660$ M^{-1} cm^{-1}) complexes have also been prepared and characterized by UV-Visible spectroscopy (where $L_3 = ms$-5,7,7, 12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane and $L_4 = rac$-Me$_6$[14]-4,11-dieneN$_4$).[19–22] The UV spectrum of $[NiL_1(NO_3)_2]ClO_4$ ($\varepsilon_{296} = 11,400$ M^{-1} cm^{-1}, $\varepsilon_{370} = 5,000$ M^{-1} cm^{-1}) in acidic aqueous solution in the presence of sulphate has been taken. ESR spectrum of the $[NiL_1]^{3+}$ complex has been taken in acidic aqueous solution in the presence of sulphate. The Ni(III) solution was prepared freshly by dissolving the sample in aqueous acidic solution containing sulphate for stabilizing the Ni(III). A stock solution of perchloric acid was prepared and was standardized by titration with potassium hydrogen phthalate. A stock solution of copper perchlorate was prepared by neutralizing copper carbonate (0.0091 mol, 2 g) with 70% perchloric acid (1.56 ml, 0.018 mol). The resultant solution was standardized iodometrically.

Caution: Compounds containing perchlorate anions must be regarded as potentially explosive and should be handled with caution.
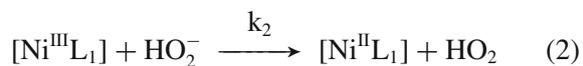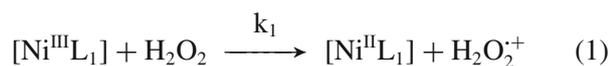
2.2 *Kinetic studies*

Studies were carried out on the kinetics of oxidation of hydrogen peroxide by $[Ni^{III}L_1]$ under second and first order conditions. The ionic strength was maintained at 0.5 mol dm^{-3} using sodium perchlorate. The pH dependence on the reaction rate was studied by varying the pH of the medium from 1–1.5 using perchloric acid. The pH was measured with an Eutech (India) instrument. The concentration of $[H_2O_2]$ was varied from 2.5×10^{-4} to 1.5×10^{-3} mol dm^{-3} and the Ni(III) complex concentration was fixed at 5×10^{-5} mol dm^{-3}. The variation of [Cu(II)] was extended over the range 5×10^{-6} to 1×10^{-4} mol dm^{-3}. The effect of sulphate on reaction rate was studied by taking its concentration as 0.002 mol dm^{-3} in the pH range 1–2.5. Absorbance changes with time were measured using a 'Shimadzu' UV-Visible recording spectrophotometer (UV-1601). Decrease in absorbance of LMCT band of Ni(III) was followed at 350 nm. The observed rate constant k_{obs} was calculated from the slopes of the linear regression plots of $\ln\{1+(Y_o-Y_\infty)\Delta_o/(Y_t-Y_\infty)[A]_o\}$ (where $\Delta_o = a[B_o]-b[A_o]$, A_o and B_o are initial concentrations of oxidant and reductant, respectively) against time for second order and $\ln(Y_t -Y_\infty)$ against time for first order conditions.[23]

3. Results and discussion

Hydrogen peroxide oxidation by $[Ni^{III}L_1]$ at pH 1–1.5 was studied in the absence of Cu(II) ion. At this pH range, hydrogen peroxide oxidation by $[Ni^{III}L_1]$ was found to be very slow. It was suggested that at very high acidic conditions the reduction of Ni(III) by the peroxy anion is slow because of its weak reducing power.[24] Uncatalysed redox reaction was observed with $[M(bipy)_3]^{3+}$, $[M(tacn)_3]^{3+}$ (where M = Ni, Fe and Ru) with evolution of oxygen.[12,13] The same trend is expected with $[Ni^{III}L_1]$. The kinetic data for the reactions of $[Ni^{III}L_1]$ complex with hydrogen peroxide are consistent with a mechanism involving the reduction

of [Ni^{III}L$_1$] by both the undissociated H_2O_2 and the peroxide anion HO_2^- (pK_a = 11.62)

$$[Ni^{III}L_1] + H_2O_2 \xrightarrow{k_1} [Ni^{II}L_1] + H_2O_2^{\cdot+} \quad (1)$$

$$[Ni^{III}L_1] + HO_2^- \xrightarrow{k_2} [Ni^{II}L_1] + HO_2 \quad (2)$$

The rate equation is given by

$$\frac{-d[Ni^{III}L_1]}{2dt} = k_1[Ni^{III}L_1][H_2O_2] + k_2[Ni^{III}L_1][HO_2^-] \quad (3)$$

$$H_2O_2 \xrightleftharpoons{K_a} H^+ + HO_2^- \quad (4)$$
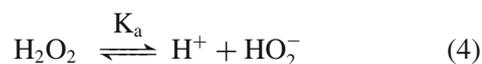
$$\begin{aligned} \frac{-d[Ni^{III}L_1]}{2dt} = {} & k_1[Ni^{III}L_1][H_2O_2] \\ & + k_2K_a[Ni^{III}L_1][H_2O_2]/[H^+] \end{aligned} \quad (5)$$

$$k = k_1 + k_2K_a/[H^+] \quad (6)$$

The negligible intercept k_1 was consistent with the small rate constant observed in acidic solution. The rate constants k_2K_a at various acid concentration were derived from the slope of k against $[H^+]^{-1}$ plot and were presented in figure 1 and table 1. With 30-fold
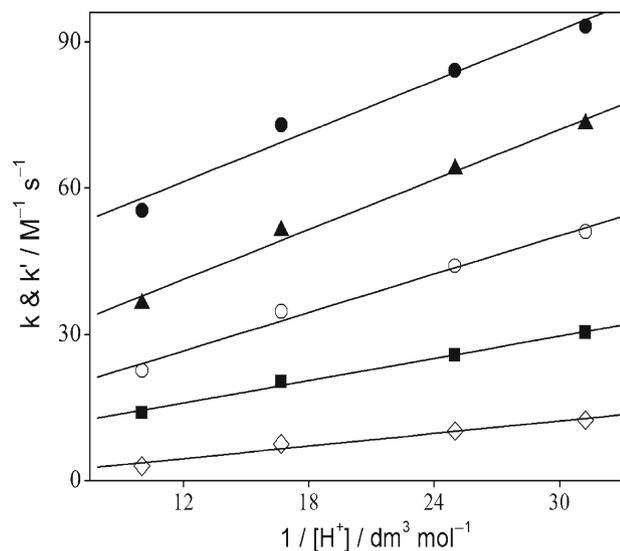

Figure 1. Plot of k and k′ against $1/[H^+]$; T = 25°C; $[H_2O_2] = 2.50 \times 10^{-4}$ mol dm^{-3}; [Ni^{III}L$_1$] = 5 × 10^{-5} mol dm^{-3}, I = 0.50 mol dm^{-3} (NaClO$_4$); [Cu(II)]/ mol dm^{-3} : ◇ − 0*; ■ −5 × 10^{-6}; ○ −1 × 10^{-5}; ▲ −5 × 10^{-5}; ● −1 × 10^{-4}; *$[H_2O_2] = 1.50 \times 10^{-3}$ mol dm^{-3}.

Table 1. Dependence of rate on pH in the absence of [Cu(II)]. [Ni^{III}L$_1$] = 5 × 10^{-5} mol dm^{-3}; $[H_2O_2] = 1.50 \times 10^{-3}$ mol dm^{-3}; T = 25°C; I = 0.50 mol dm^{-3} (NaClO$_4$).

pH	k / dm^3 mol^{-1} s^{-1}	$k_2K_a/[H^+]$
1.0	2.96 ± 0.04 (4.29)	4.29
1.2	7.51 ± 0.03 (7.16)	7.16
1.4	10.2 ± 0.02 (10.7)	10.7
1.5	12.4 ± 0.03 (13.4)	13.4

Numbers in parentheses are values calculated with use of (6).

increase in concentration of hydrogen peroxide, the rate constants displayed an inverse dependence on the acid concentration. Oxygen evolution occurs but the reduction of metal centre was not observed completely. This complication may be due to the formation of stable [Ni^{III}L$_1$HO$_2^-$] (eq. 7), which acts as strong oxidant than [Ni^{III}L$_1$], and the oxidation of cyclam ligand.

$$[Ni^{III}L_1] + HO_2^- \rightleftharpoons [Ni^{III}L_1HO_2^-] \quad (7)$$
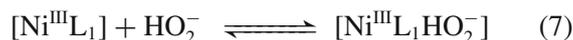
The decomposition pathway for the superoxide ions formed by reactions (1) an (2) are given by (8) and (9) respectively.[13]

$$H_2O_2^{\cdot+} \rightleftharpoons H^+ + HO_2^{\cdot} \quad (8)$$

$$2HO_2^{\cdot} \longrightarrow H_2O_2 + O_2 \quad (9)$$
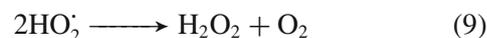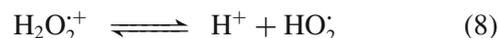
In the presence of Cu(II), the metal centre reduction takes place more rapidly when compared with cyclam ligand oxidation. Most of the reactions involving hydrogen peroxide are carried out at higher pH (pH > 5) and HO_2^- is responsible for the decomposition of H_2O_2. It is obvious that the oxidation of H_2O_2 by Cu(II) is more favourable in alkaline medium and the rate of decomposition of H_2O_2 by Cu(II) alone at low pH is considered negligible compared with the decomposition of H_2O_2 by [Ni^{III}L$_1$] complex. Interaction of Cu(II) with [Ni^{III}L$_1$] complexes in aqueous acidic condition was ruled out.[25]

The Cu(II) ion catalysed oxidation of H_2O_2 by [Ni^{III}L$_1$] complex, in the pH range 1 < pH < 1.5 studied, was found to be fast. The second order rate constants at various [Cu(II)] ranging from 5 × 10^{-6} to 1 × 10^{-4} mol dm^{-3} showed an inverse dependence on the acid concentration (table 2).
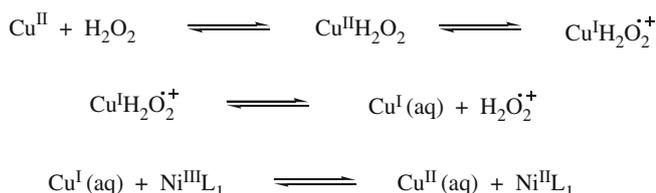
It was also pointed out that the promoting action of Cu(II) ions has been considered due to their ready reducibility to transient Cu(I) ions. In this redox reaction, oxygen evolution takes place which suggests the formation of copper–peroxo complexes.[26–30] In aqueous medium, formation of highly labile species (eq. 10) and

Table 2. Dependence of rate on [Cu(II)] at various pH. $[Ni^{III}L_1] = 5 \times 10^{-5}$ mol dm^{-3}; $[H_2O_2] = 2.50 \times 10^{-5}$ mol dm^{-3}; T = 25°C; I = 0.50 mol dm^{-3} (NaClO$_4$).

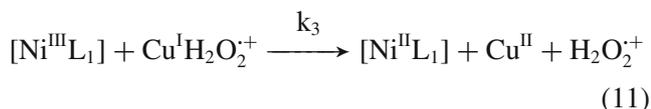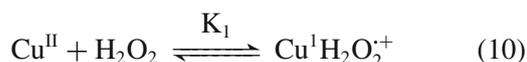| pH	[Cu(II)] / mol dm^{-3}	k' / dm^3 mol^{-1} s^{-1}	$k_b K_a$/ [H$^+$]
1.0	5×10^{-6}	13.9 ± 0.03 (14.4)	7.61
	1×10^{-5}	22.6 ± 0.04 (24.0)	13.1
	5×10^{-5}	36.3 ± 0.05 (37.9)	17.1
	1×10^{-4}	55.4 ± 0.02 (57.9)	17.3
1.2	5×10^{-6}	20.3 ± 0.04 (19.5)	12.7
	1×10^{-5}	34.7 ± 0.02 (32.8)	21.9
	5×10^{-5}	51.3 ± 0.02 (49.2)	28.4
	1×10^{-4}	72.9 ± 0.03 (69.4)	28.8
1.4	5×10^{-6}	25.7 ± 0.03 (25.8)	19.0
	1×10^{-5}	44.1 ± 0.05 (43.7)	32.8
	5×10^{-5}	63.9 ± 0.03 (63.4)	42.6
	1×10^{-4}	84.1 ± 0.04 (83.8)	43.1
1.5	5×10^{-6}	30.4 ± 0.03 (30.6)	23.7
	1×10^{-5}	51.0 ± 0.05 (51.9)	41.0
	5×10^{-5}	73.2 ± 0.02 (74.1)	53.3
	1×10^{-4}	93.2 ± 0.02 (94.6)	53.9

Numbers in parentheses are values calculated with use of (17).

successive electron transfer reaction with $[Ni^{III}L_1]$ may be given in the following scheme 2.

$$Cu^{II} + H_2O_2 \rightleftharpoons Cu^{II}H_2O_2 \rightleftharpoons Cu^{I}H_2O_2^{\cdot+}$$

$$Cu^{I}H_2O_2^{\cdot+} \rightleftharpoons Cu^{I}(aq) + H_2O_2^{\cdot+}$$

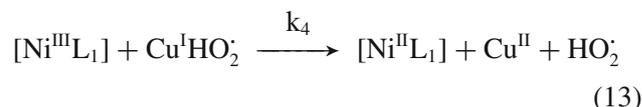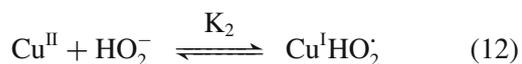$$Cu^{I}(aq) + Ni^{III}L_1 \rightleftharpoons Cu^{II}(aq) + Ni^{II}L_1$$

Scheme 2. Equilibrium pathways for the interaction of copper(II) ion with hydrogen peroxide.

The rate expression for Cu(II) catalysed hydrogen peroxide oxidation may be written as shown in equation 11.

$$Cu^{II} + H_2O_2 \underset{}{\overset{K_1}{\rightleftharpoons}} Cu^{I}H_2O_2^{\cdot+} \quad (10)$$

$$[Ni^{III}L_1] + Cu^{I}H_2O_2^{\cdot+} \xrightarrow{k_3} [Ni^{II}L_1] + Cu^{II} + H_2O_2^{\cdot+} \quad (11)$$

The peroxy anion might react with both Cu(II) and $[Ni^{III}L_1]$. The $[Ni^{III}L_1HO_2^-]$ formed is a stable oxidant and the preferable reaction pathway involves interaction of $[Cu^{II}HO_2^-]$ with $[Ni^{III}L_1]$. The possible equilibrium may be represented by the following sequence, scheme 3.

The rate equation for the Cu(II) ion promoted peroxy anion may be given by the equation 13.

$$Cu^{II} + HO_2^- \underset{}{\overset{K_2}{\rightleftharpoons}} Cu^{I}HO_2 \quad (12)$$

$$[Ni^{III}L_1] + Cu^{I}HO_2 \xrightarrow{k_4} [Ni^{II}L_1] + Cu^{II} + HO_2 \quad (13)$$

The rate expression involving uncatalysed and catalysed hydrogen peroxide oxidation by $[Ni^{III}L_1]$ is shown by the following rate equations:
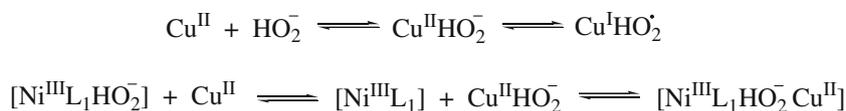
$$\frac{-d[Ni^{III}L_1]}{2dt} = k_1[Ni^{III}L_1][H_2O_2]$$
$$+ k_2[Ni^{III}L_1][HO_2^-]$$
$$+ k_3[Ni^{III}L_1][Cu^{I}H_2O_2^{\cdot+}]$$
$$+ k_4[Ni^{III}L_1][Cu^{I}HO_2^{\cdot}] \quad (14)$$

$$\frac{-d[Ni^{III}L_1]}{2dt} = k_1[Ni^{III}L_1][H_2O_2]$$
$$+ k_2K_a[Ni^{III}L_1][H_2O_2]/[H^+]$$
$$+ k_3K_1[Ni^{III}L_1][H_2O_2][Cu^{II}]$$
$$+ k_4K_2K_a[Ni^{III}L_1][H_2O_2][Cu^{II}]/[H^+] \quad (15)$$

$$k' = (k_1 + k_3K_1[Cu^{II}])$$
$$+ K_a(k_2 + k_4K_2[Cu^{II}])/[H^+] \quad (16)$$

$$k' = k_a + k_bK_a/[H^+] \quad (17)$$

where k_a $(= k_1 + k_3K_1[Cu^{II}])$ was obtained from intercept and k_bK_a $(k_b = k_2 + k_4K_2[Cu^{II}]$ was obtained from

$$Cu^{II} + HO_2^- \rightleftharpoons Cu^{II}HO_2^- \rightleftharpoons Cu^IHO_2^\cdot$$

$$[Ni^{III}L_1HO_2^-] + Cu^{II} \rightleftharpoons [Ni^{III}L_1] + Cu^{II}HO_2^- \rightleftharpoons [Ni^{III}L_1HO_2^-Cu^{II}]$$

Scheme 3. Equilibrium pathways for the interaction of copper(II) ion with peroxy anion.

slope of k′ against $[H^+]^{-1}$ plot (figure 1). Activation of H_2O_2 increases by increasing the [Cu(II)] and was observed by the increase in the rate constant (table 2). The influence of copper(II) ions on reaction kinetics was observed from the plot of log k′ against log[Cu^{II}] with a slope of 0.44 at pH 1 (figure 2).

3.1 *Sulphate dependence*

Between the pH 1 and 2.5, the oxidation kinetics was studied at sulphate ion concentration of 0.002 mol dm^{-3} and copper(II) ion concentration of 1×10^{-4} mol dm^{-3}. Variation of sulphate ion concentration at constant pH 2 has also been studied. In the presence of sulphate, the rate constant is found to decrease.

In sulphate medium, [Ni^{III}L$_1$] exist as sulphato–complex according to the equation 18. The factors such as stabilization of the complex by hydrogen bonding and the lower reduction potential[21] of [NiL$_1$(SO$_4$)]$^+$ are considered to retard the hydrogen peroxide oxidation in the presence of sulphate. Also formation of copper sulphate which is a weak catalyst might reduce the availability of free Cu(II) towards the promoting action.
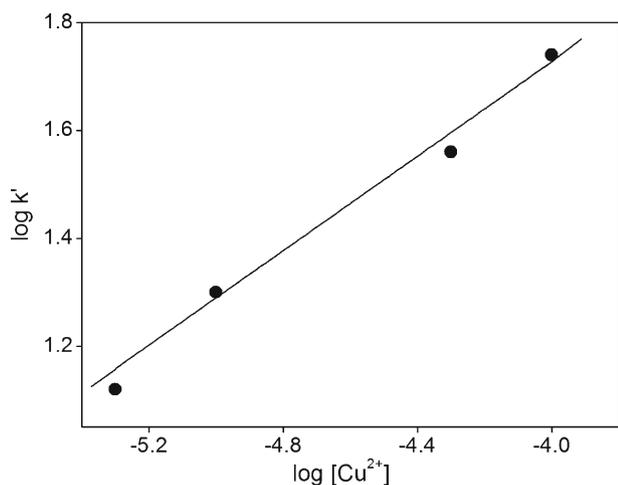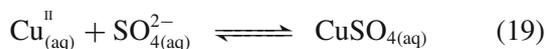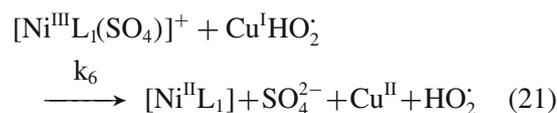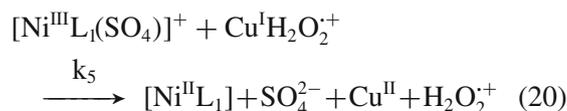
$$[Ni^{III}L_1]^{3+} + SO_4^{2-} \xrightleftharpoons{K_f} [Ni^{III}L_1SO_4]^+ \quad (18)$$

$$Cu^{II}_{(aq)} + SO_{4(aq)}^{2-} \rightleftharpoons CuSO_{4(aq)} \quad (19)$$

Figure 2. Plot of logk′ against 1/[H$^+$]; T = 25°C; [H$_2$O$_2$] = 2.5×10^{-4} mol dm^{-3}; [complex] = 5×10^{-5} mol dm^{-3}; I = 0.50 mol dm^{-3} (NaClO$_4$), pH = 1.

In the presence of sulphate and Cu(II) ion, the kinetic pathways (20) and (21) are presented.

$$[Ni^{III}L_1(SO_4)]^+ + Cu^IH_2O_2^{\cdot+}$$
$$\xrightarrow{k_5} [Ni^{II}L_1] + SO_4^{2-} + Cu^{II} + H_2O_2^{\cdot+} \quad (20)$$

$$[Ni^{III}L_1(SO_4)]^+ + Cu^IHO_2^\cdot$$
$$\xrightarrow{k_6} [Ni^{II}L_1] + SO_4^{2-} + Cu^{II} + HO_2^\cdot \quad (21)$$

The overall rate expression including uncatalysed (eq. 1, 2) catalysed (11, 13) and the presence of sulphate (eq. 20, 21) for the oxidation of H_2O_2 by [Ni^{III}L$_1$] may involve the following steps:

$$\begin{aligned}
\frac{-d[Ni^{III}L_1]}{2dt} &= k_1[Ni^{III}L_1][H_2O_2] \\
&\quad + k_3K_1[Ni^{III}L_1][H_2O_2][Cu^{II}] \\
&\quad + k_5K_fK_1[Ni^{III}L_1][SO_4][H_2O_2][Cu^{II}] \\
&\quad + k_2K_a[Ni^{III}L_1][H_2O_2]/[H^+] \\
&\quad + k_4K_2K_a[Ni^{III}L_1][H_2O_2][Cu^{II}]/[H^+] \\
&\quad + k_6K_2K_fK_a[Ni^{III}L_1][SO_4][H_2O_2][Cu^{II}]/[H^+]
\end{aligned}$$
$$(22)$$

$$\begin{aligned}
k'' &= (k_1 + k_3K_1[Cu^{II}] + k_5K_1K_f[Cu^{II}][SO_4]) \\
&\quad + K_a(k_2 + k_4K_2[Cu^{II}] \\
&\quad + k_6K_fK_2[Cu^{II}][SO_4])/[H^+]
\end{aligned} \quad (23)$$

$$k'' = k_c + k_dK_a/[H^+] \quad (24)$$

In the rate law equation 24, $k_c(= k_1 + k_3K_1[Cu^{II}] + k_5K_1K_f[Cu^{II}][SO_4])$ and $k_dK_a(k_d = k_2 + k_4K_2[Cu^{II}] + k_6K_fK_2[Cu^{II}][SO_4])$ were obtained from intercept and slope of the plot of k″ against $[H^+]^{-1}$, respectively (figure 3 and table 3).

3.2 *Interpretation of ligand oxidation*

In order to confirm the involvement of HO$_2^-$ with Ni(III) centre and oxidation of ligand by ·OH radical, the
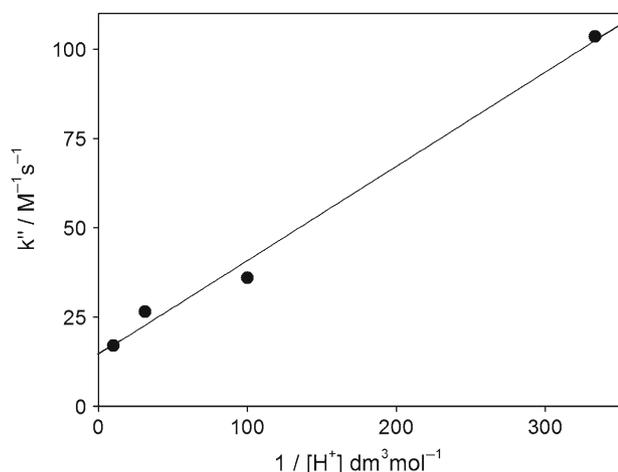
Figure 3. Plot of k'' against $1/[H^+]$; $T = 25°C$; $[H_2O_2] = 2.5 \times 10^{-4}$ mol dm^{-3}; [complex] $= 5 \times 10^{-5}$ mol dm^{-3}; $I = 0.50$ mol dm^{-3} (NaClO$_4$), [Cu(II)] $= 1 \times 10^{-4}$ mol dm^{-3}; [Na$_2$SO$_4$] $= \bullet - 0.002$ mol dm^{-3}.
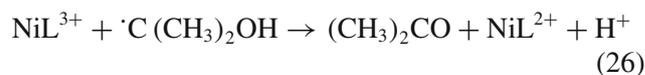
reaction was interpreted on the basis of the observations from the following reactions:

3.2a *Study of the reaction of $\cdot$OH radical*: Spectral scans of metal centred reduction of $[Ni^{III}L_1]$ was studied under first order conditions (20-fold of H_2O_2) both in the presence and absence of Cu(II) and in the presence of sulphate at pH1. After the complete disappearance of LMCT band of $[Ni^{III}L_1]$ at 300 nm, the increases in the intense peak at 284 nm and at 522 nm with development of pink colour was observed (figure 4a). Similar observations were made with $[NiL_1]^{2+}$ in the present study. McAuley suggested that it was due to the transient Ni(III)(hydroxo)ion and the hydroxyl radical[17] which leads to diimine followed by the formation of pink dimeric species. The crystal structure of $[NiL_1(NO_3)_2](NO_3)$ showed the cyclam to be in a *trans*-III conformation with the two secondary amines of the six-member ring *cis* to each other. This configuration would permit dehydrogenation in the ring.

In the spectral scans of the oxidation of $[NiL_2](ClO_4)_2$ (L$_2$ = 1,8-bis(2-hydroxyethyl)-1,3,6, 8,10,13-hexaazacyclotetradecane) by hydrogen peroxide both in the absence and presence of Cu(II) and in the presence of sulphate at pH1 no such pink species with an intense peak at 520 nm was observed (figure 4b). Instead, a peak at 270 nm and a shoulder near 325 nm were formed rapidly. The intensity of the shoulder at 325 nm gradually decreases and reaches a limit at 270 nm.

Hydrogen peroxide has no effect on both $[NiL_3](ClO_4)_2$ and $[NiL_4](ClO_4)_2$. The CTTS band of these complexes was affected only slightly. From the UV spectrum of $[NiL_4](ClO_4)_2$, it was found that the peak formed at 280 nm of $[NiL_2]^{2+}$ and 270 nm of $[NiL_1](ClO_4)_2$ by reaction with hydrogen peroxide may be due to $\pi \rightarrow \pi^*$ transition of C=N. Therefore, it may be concluded that the reaction of Ni(III) complex with hydrogen peroxide is accompanied by abstraction of 'H' atom from the macrocyclic ligand. But in the presence of Cu(II), reduction of Ni(III) to Ni(II) is faster than the abstraction of H atom.

3.2b *Effect of isopropyl alcohol*: The involvement of $\cdot$OH radical can be understood by carrying out the kinetics of oxidation of hydrogen peroxide by Ni(III) complex in the presence of 2-propanol. The $\cdot$OH radical tend to abstract hydrogen both from macrocylic ligand and isopropyl alcohol.

$$HC(CH_3)_2OH + \cdot OH \rightarrow \cdot C(CH_3)_2\,OH + H_2O \quad (25)$$

$$NiL^{3+} + \cdot C\,(CH_3)_2OH \rightarrow (CH_3)_2CO + NiL^{2+} + H^+ \quad (26)$$

The plot of k'' against [isopropyl alcohol] (table 4, figure 5) was linear with a positive slope and there is no effect up to an isopropyl alcohol concentration of 1 mol dm^{-3}. Since the reaction of HO_2^- is faster than $\cdot$OH,[31] the promoting action of Cu(II) ion is not affected in the

Table 3. Dependence of rate on sulphate. [Complex] $= 5 \times 10^{-5}$ mol dm^{-3}; $[H_2O_2] = 2.50 \times 10^{-5}$ mol dm^{-3}; $T = 25°C$; [Cu(II)] $= 1 \times 10^{-4}$ mol dm^{-3}; $I = 0.50$ mol dm^{-3} (NaClO$_4$).

	[Na$_2$SO$_4$] 0.002 mol dm^{-3}		pH 2	
pH	k'' / dm^3 mol^{-1} s^{-1}	$k_d K_a/ [H^+]$	$[SO_4^{2-}]$ mol dm^{-3}	k'' / dm^3 mol^{-1} s^{-1}
1.0	17.0 ± 0.02 (17.2)	2.63	0.001	52.0 ± 0.04
1.5	26.5 ± 0.03 (22.8)	8.23	0.002	36.0 ± 0.03
2.0	36.0 ± 0.03 (40.9)	26.3	0.005	26.3 ± 0.06
2.5	104 ± 0.01 (102)	87.7		

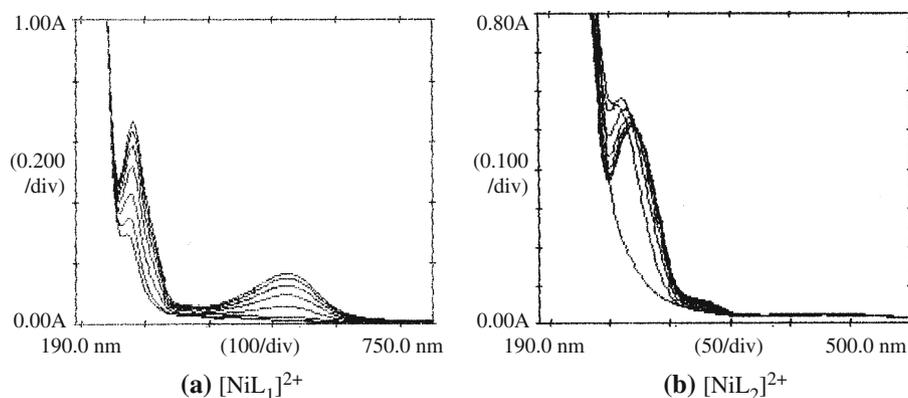Numbers in parentheses are values calculated with use of (24).

Figure 4. Spectral scans observed for the oxidation of macrocyclic ligands (L = L_1 and L_2) of Ni(II) complexes by hydrogen peroxide: [NiL]$^{2+}$ complexes = 2 × 10^{-4} mol dm^{-3}; [Na$_2$SO$_4$] = 0.001 mol dm^{-3}; [H$_2$O$_2$] = 4 × 10^{-3} mol dm^{-3}; pH = 1(HClO$_4$); I = 0.50 mol dm^{-3} (NaClO$_4$). Scans (**a**) and (**b**) measured at 900 s intervals in the absence of Cu(II).

oxidation of H$_2$O$_2$ than the interaction of ˙OH radical with macrocyclic complex in acidic medium. The interaction of ˙OH is observed after the reduction of Ni(III) centre. It was suggested that H$_2$O$_2$ reacts with NiL^{2+} by a Fenton-type mechanism. Therefore, the effect of isopropyl alcohol at lower concentration has not been observed.

It was hence concluded that the HO$_2^-$ would be the reacting species rather than ˙OH radical. The rate of decomposition of Ni(III) complex is enhanced especially in the presence of isopropyl alcohol concentration above 1 mol dm^{-3}. This is because, in addition to catalysis by Cu(II), α-hydroxy alkyl radical which is formed from alcohol by reacting with ˙OH, may also react with Ni(III) and thus responsible for enhanced decomposition of Ni(III).[32] After the reduction of Ni(III) to Ni(II), the suppression of the peak at 520 nm was observed without affecting the peak at 270 nm. This suggests that the peak produced at 270 nm is not due to true Ni(III), but may be a transient species.

3.2c *Reaction of t-Butyl hydroperoxide with Ni(II) macrocyclic complexes*: Oxidation of [NiL$_1$](ClO$_4$)$_2$ at pH1 using excess *t*-BuOOH in the presence of sulphate concentration of 0.10 mol dm^{-3} displayed ligand to metal charge transfer (LMCT) band at 300 nm and charge transfer to solvent (CTTS) band at 220 nm with an isosbestic point at 242 nm. The pseudo-first order rate constant, k$_{obs}$, was found to be 2.42 × 10^{-4} s^{-1}. In the presence of sulphate, the nickel(III) produced in the reaction of [NiL$_1$]$^{2+}$ with *t*-BuO˙ was stable. With [NiL$_2$](ClO$_4$)$_2$, the appearance of an intense band (LMCT) at 290 nm in the presence of sulphate ion suggests the formation of Ni(III) at the same reaction

Table 4. Effect of isopropyl alcohol on rate constant at pH = 1: [Ni^{III}L$_1$] = 5 × 10^{-5} mol dm^{-3}; [H$_2$O$_2$] = 5 × 10^{-4} mol dm^{-3}; T = 25°C; [Cu(II)] = 1 × 10^{-4} mol dm^{-3}; [Na$_2$SO$_4$] = 0.002 mol dm^{-3}; I = 0.50 mol dm^{-3} (NaClO$_4$).

[Isopropyl alcohol] / mol dm^{-3}	k″ / dm^3 mol^{-1} s^{-1}
1.0	17.0 ± 0.07
1.5	21.5 ± 0.10
2.0	25.7 ± 0.05
2.5	28.9 ± 0.10
3.0	32.5 ± 0.10
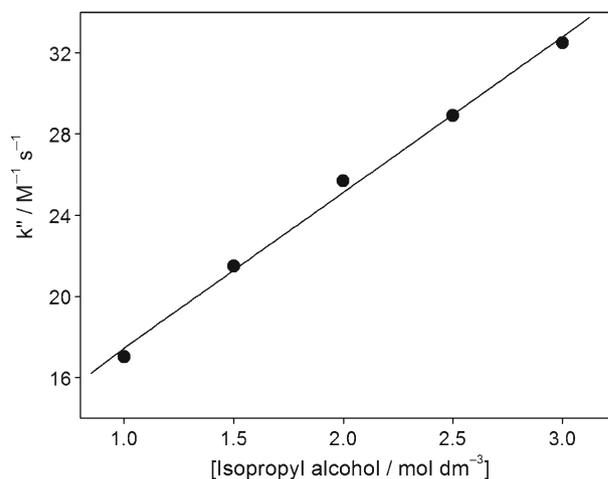
Figure 5. Effect of isopropyl alcohol on rate constant: [Ni^{III}L$_1$] = 5 × 10^{-5} mol dm^{-3}; pH = 1 (HClO$_4$); [Na$_2$SO$_4$] = 0.002 mol dm^{-3}; Temp = 25°C; I = 0.50 mol dm^{-3} (NaClO$_4$); [Cu(II)] = 1 × 10^{-4} mol dm^{-3}; [H$_2$O$_2$] = 5 × 10^{-4} mol dm^{-3}.

Table 5. Rate constants for the oxidation of $[NiL]^{2+}$ (L = L_1, L_2, L_3 and L_4) by *t*-Butyl hydroperoxide at 25°C: $[NiL]^{2+} = 5 \times 10^{-5}$ mol dm^{-3}, $[Na_2SO_4] = 0.10$ mol dm^{-3}, pH = 1(HClO$_4$), [*t*-BuOOH] = 5×10^{-3} mol dm^{-3}, I = 0.50 mol dm^{-3} (NaClO$_4$).

Complex	$k_{obs}/10^{-4}$, s^{-1}
$[NiL_1]^{2+}$	2.42 ± 0.04
$[NiL_2]^{2+}$	2.18 ± 0.02
$[NiL_3]^{2+}$	Very slow
$[NiL_4]^{2+}$	No reaction

conditions. During the reaction, the other charge transfer band at 210 nm (CTTS) decreased in intensity with time, showing an isobestic point at 240 nm.

A metal centre oxidation of the $[NiL_3](ClO_4)_2$ complex was very slow with *t*-BuOOH with an increase in LMCT band at 409 nm and 310 nm and decreases in the CTTS band at 236 nm. *t*-BuOOH has no action on $[NiL_4](ClO_4)_2$. Therefore, it was concluded that the *t*-BuO· would not attack the macrocyclic ligand.

On the basis of the reaction of the above complexes with *t*-BuOOH, it was concluded that for the Ni(II) complexes of macrocyclic ligands I–III, the metal centred oxidation takes place, the rates being in the order NiL$_1$ > NiL$_2$ > NiL$_3$ (scheme 1, table 5). With H$_2$O$_2$, ligand oxidation of macrocyclic ring takes place with complexes I and II in which hydrogen atom of secondary nitrogen can be easily abstracted by ·OH.

From these studies, in the oxidation of $[NiL_1](ClO_4)_2$ by H$_2$O$_2$, in addition to increase in peak at 280 nm, the

progress of the peak at 520 nm suggest the formation of tetraene form of dimer by removal of an α-hydrogen. In the case of $[NiL_2](ClO_4)_2$, the α-position is strained due to the uncoordinated bridge head nitrogen (N1 and N8) with hydroxyethyl substituent so that it forms only dienes.

3.3 *Correlation with Marcus theory*

According to the modified form of Marcus theory,[33] the rate constant for a cross-reaction k_{12} is related to the rate constants for the component exchange reactions k_{11} and k_{22} and the equilibrium constant for the cross-reaction K_{12} by

$$k_{12} = (k_{11}k_{22}k_{12}f_{12})^{1/2} W_{12}, \qquad (27)$$

where

$$\ln f_{12} = \frac{[\ln K_{12} + (W_{12} - W_{21})/RT]^2}{4[\ln(k_{11}k_{22}/A_{11}A_{22}) + ((W_{11} + W_{22})/RT)]}$$

$$W_{12} = \exp[-(W_{12} + W_{21} - W_{11} - W_{22})/2RT]$$

$$W_{ij} = e^2 z_i z_j/D_s \sigma_{ij}(1 + \beta\sigma_{ij}I^{1/2})$$

$$A_{ii} = \left[\frac{4\pi N\sigma^2 vb\gamma r}{1000}\right]_{ii}.$$

In these expressions W_{ij} is the work required to bring ions i and j (charges z_i and z_j) to the separation distance σ_{ij} (taken equal to the sum of a_i and a_j, the radii of ions i and j), $\beta = (8\pi Ne^2/1000D_s kT)^{1/2}$, and D_s is the dielectric constant of the medium, vb is the nuclear

Table 6. Cross-reaction and self-exchange rate constants for reactions involving the HO$_2^-$/HO$_2$ couple; ionic strength in parentheses. [13,26]

S. No.	Oxidant[a]	E°(V)	k_{22} (M^{-1} s^{-1})[b]	k_2 (M^{-1}s^{-1})
I	Os(dmbpy)$_3^{3+}$	0.66	4.2×10^8 (0.1)[c]	1.00×10^3 (0.5)
II	Os(bpy)$_3^{3+}$	0.81	4.2×10^8 (0.1)[c]	6.00×10^3 (0.5)
III	Fe(dmbpy)$_3^{3+}$	0.81	3.0×10^8 (5.5)	2.70×10^4 (0.5)
IV	Fe(bpy)$_3^{3+}$	1.05	3.0×10^8 (5.5)	7.10×10^5 (0.5)
V	Ru(dmbpy)$_3^{3+}$	1.06	4.2×10^8 (0.1)	1.30×10^6 (0.5)
VI	Ru(bpy)$_3^{3+}$	1.26	4.2×10^8 (0.1)	2.40×10^7 (0.5)
VI	Ni(dmbpy)$_3^{3+}$	1.59	1.5×10^3 (1.0)	3.30×10^7 (0.5)
VIII	Ni(bpy)$_3^{3+}$	1.72	1.5×10^3 (1.0)	2.40×10^8 (0.5)
IX	Fe(ttcn)$_2^{3+}$	1.44	6.7×10^6 (0.5)	2.63×10^9 (0.1)
X	Ni(tacn)$_2^{3+}$	0.95	6.0×10^3 (1.0)	6.15×10^6 (0.1)
XI	Ni^{III}L$_1$	0.97	2.0×10^3 (1.0)	1.79×10^{11} (0.5)**

[a]dmbpy = 4,4'-(CH$_3$)$_2$bpy; py = pyridine; tacn = (1,4,7-triazacyclononane); ttcn = (1,4,7-trithiacyclononane)
[b]Self-exchange rate constants: k_{22} is for partner of HO$_2^-$ or HO$_2$ in cross-reaction
[c]k_{22} for OsL$_3^{2+/3+}$ is assumed to be the same as for Ru(bpy)$_3^{2+/3+}$
k_2 = rate constant for cross reaction; ** - present work in the absence of [Cu(II)] and [SO$_4^{2-}$]
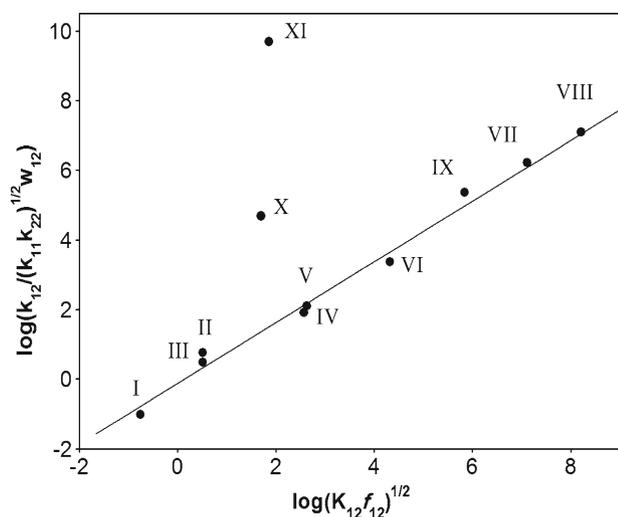
Figure 6. Plot of $\log k_{12}/(k_{11}k_{22})^{1/2}W_{12}$ vs. $\ln[(K_{12}f_{12})^{1/2}]$; The Roman numbers denote that each circle represents the reaction of HO_2^- with: $Os(dmbpy)_3^{3+}$, I; $Os(bpy)_3^{3+}$, II; $Fe(dmbpy)_3^{3+}$, III; $Fe(bpy)_3^{3+}$, IV; $Ru(dmbpy)_3^{3+}$, V; $Ru(bpy)_3^{3+}$, VI; $Ni(dmbpy)_3^{3+}$, VII; $Ni(bpy)_3^{3+}$, VIII; $Fe(ttcn)_2]^{3+}$, IX; $Ni(tacn)_2^{3+}$, X; $Ni^{III}L_1$, XI. The points are calculated using k_{11} for $HO_2^-/HO_2 = 5 \times 10^{-2}$ $M^{-1}s^{-1}$.

frequency that destroys the activated complex configuration ($\sim 9 \times 10^{12}$ s^{-1}), and γr is the thickness of the reaction layer (typically ~ 0.8 Å). Value of A/σ^2 for the Ni(III) complex has been taken as 4.8×10^{10} M^{-1} Å^{-2} s^{-1} and the value of $A_{11}A_{22}$ for the ML_3^{3+}/HO_2^- reactions is taken as 2×10^{24} M^{-2}s^{-2}. The radii of the $[NiL_1]^{3+}$ and the peroxide anion are 5.0 Å and 1.6 Å, respectively.[12,34]

The redox potential of HO_2 is taken as 0.75 V.[28] With $k_{11} = 5 \times 10^{-2}$ M^{-1}s^{-1}, the plot of log $(k_{12}/(k_{11}k_{22})^{1/2}W_{12})$ against $\log(K_{12}f_{12})^{1/2}$ indicates that the rate constants k_2 for the oxidation of HO_2^- increase as the reduction potentials of the oxidants in the series is increased except of $[Ni(tacn)_2]^{3+}$ and $[NiL_1]^{3+}$ complexes (table 6 and figure 6). Similar to $[Ni(tacn)_2]^{3+}$, interaction of $[Ni^{III}L_1]$ with HO_2^- is represented by the following scheme 4.[13]

The rate constant for the oxidation of HO_2^- by $[Ni^{III}L_1]$ is greater than that predicted by outer sphere reactions.
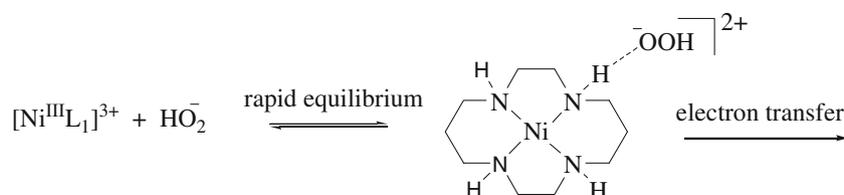
3.4 *Estimation of hydrogen peroxide*

An attempt has been made to estimate the amount of hydrogen peroxide remaining in the solution after oxidation of hydrogen peroxide by $[Ni^{III}L_1]$ complex.[35,36]

A reagent solution containing xylenol orange (XO) (5×10^{-4} mol dm^{-3}) and Fe(II) ammonium sulphate (2×10^{-4} mol dm^{-3}) was prepared in perchloric acid medium. The resultant pH of the solution was adjusted to pH 1.8. The H_2O_2 (5×10^{-5} mol dm^{-3}) was added to the solution and the volume of the solution was made up to 5 ml. The absorbance was measured at 550 nm against blank. The concentration of the H_2O_2 was calculated using the extinction coefficient 2.68×10^4 M^{-1} cm^{-1}.

Oxidation of H_2O_2 by $[Ni^{III}L_1]$ at pH 1.5 was studied in the absence of sulphate with [Cu(II)] of 1×10^{-4} mol dm^{-3}. The ratio of Ni(III): H_2O_2 was 1:5. As soon as the absorbance λ_{max} due to Ni(III) disappear 1 ml of the reaction mixture was pipetted out immediately and was added to the reagent mixture containing xylenol orange of the resulting pH 1.8 (HClO$_4$). Then the absorbance was measured against blank. The concentration of the resultant H_2O_2 was found to be 4.3×10^{-5} mol dm^{-3}. This result suggests a stoichiometry of 2:1 for the reaction. The slight decrease in resultant concentration may be an error or may due to the reaction of ˙OH radical by the Ni(II) formed as product of reduction of Ni(III).

Thus, the copper catalysed oxidation of hydrogen peroxide by $[Ni^{III}L_1]$ reaction is mainly due to the HO_2^- ion rather than the reaction of ˙OH radical.

4. Conclusions

In summery, the kinetics of oxidation of hydrogen peroxide by $[Ni(cyclam)]^{3+}$ shows that the reaction is catalysed by the presence of Cu(II) ion in acidic aqueous solution and is faster in the presence of Cu(II) ion than in its absence. The reduction of the metal centre is faster than the cyclam ligand oxidation to form tetraene by peroxide ion.

Scheme 4. Mode of electron transfer between $[Ni^{III}L_1]$ and peroxy anion.

References

1. Evans M G, George P and Uri N 1949 *Trans. Faraday Soc.* **45** 230
2. Jones P, Kitching R, Tobe M L and Wynne Jones W F K 1959 *Trans. Faraday Soc.* **55** 79
3. Kremer M L and Stein G 1959 *Trans. Faraday Soc.* **55** 959
4. Wells C F and Fox D 1976 *J. Inorg. Nucl. Chem.* **38** 107
5. Wells C F and Husain M 1970 *J. Chem. Soc.* **(A)** 1013
6. Wells C F and Mays D 1968 *J. Chem. Soc.* **(A)** 665
7. Baxendale J H and Wells C F 1957 *Trans. Faraday Soc.* **53** 800
8. Wells C F and Husain M 1971 *Trans. Faraday Soc.* **67** 760
9. Wells C F and Mays D 1969 *Inorg. Nucl. Chem. Lett.* **5** 9
10. Sharma V K, Millero F J and Homonnay Z 2004 *Inorg. Chim. Acta* **357** 3583
11. Wells C F and Fox D 1977 *J. Chem. Soc. Dalton Trans.* **1498**
12. Macartney D H 1986 *Can. J. Chem.* **64** 1936
13. Koshino N, Funahashi S and Takagi H D 1997 *J. Chem. Soc. Dalton Trans.* 4175
14. McAuley A and Xu C 1992 *Inorg. Chem.* **31** 5549
15. Whitburn K D and Laurence G S, 1979 *J Chem. Soc. Dalton Trans.* 139
16. Xavier Solans-Monfort, Jose Lis G Fierro, Lara Hermosilla, Carlos Sieiro, Mariona Sodpe and Ruben Mas-Balleste 2011 *Dalton Trans.* **40** 6868
17. Barefield E K, Wagner F, Herlinger A W and Dahl A R 1976 *Inorg. Synth.* **16** 222
18. McAuley A, Palmer T A and Whitcombe T W 1993 *Can. J. Chem.* **71** 1792
19. Suh M P, Shim B Y and Yoon T 1994 *Inorg. Chem.* **33** 5509
20. Tait A M and Busch D H 1972 *Inorg. Nucl. Chem. Lett.* **8** 491
21. Cohen H, Krischenbaum L J, Zeigerson E, Jaacobi M, Fuchs E, Ginsbrg G and Meyerstein D 1979 *Inorg. Chem.* **18** 2763
22. Jaacobi M, Meyerstein D and Lilie J 1979 *Inorg. Chem.* **18** 429
23. Espenson J H 1995 *Chemical kinetics and reaction mechanisms*, 2nd edition, McGraw-Hill
24. Meshulam A, Cohen H and Meyerstein D 1998 *Inorg. Chim. Acta* **273** 266
25. Ariela Brg, Eric Maimon, Haim Cohen and Dan Meyerstein 2007 *Eur. J. Inorg. Chem.* **530**
26. Cheves Walling and Andre Goosen 1973 *J. Am. Chem. Soc.* **95** 2987
27. Haber F and Weiss J 1934 *J. Proc. R. Soc. (London)* **A147** 332
28. Barb W G, Baxendale J H, George P and Harorave K R 1951 *Trans Faraday Soc.* **47** 591
29. Mordechai L Kremer 1962 *J. Catal.* **1** 351
30. Pecci L, Montefoschi G and Cavallini D 1997 *Biochem. Biophy. Res. Commun.* **235** 264
31. Rabani J, Klug-Roth D, Lilie J 1973 *J. Phy. Chem.* **77** 1169
32. Yao Q, Bakac A, Espenson J H 1993 *Inorg. Chem.* **32** 1488
33. Sutin N 1982 *Acc. Chem. Res.* **15** 275; 1983 *Prog. Inorg. Chem.* **30** 441
34. Macartney D H and Sutin N 1983 *Inorg. Chim. Acta* **74** 221
35. Gupta B L 1973 *J. Microchem.* **18** 363
36. Gay C, Collins J and Gebicki J M 1999 *Anal. Biochem.* **273** 149