Kinetics of oxidation of nickel(II) aza macrocycles by peroxydisulphate in aqueous media

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Abstract. The kinetics of the oxidation of nickel (II) hexaaza and nickel (II) pentaaza macrocycles by the peroxydisulphate anion, $S_2O_8^{2-}$, were studied in aqueous media. Effect of *p*H on reaction rate was also studied. The rate increases with increase of $S_2O_8^{2-}$ concentration. Rates are almost independent of acid between *p*H 4 and 2, giving overall a relatively simple second-order rate law followed by oxidation within the ion pair solvent shell. Using rate $= +1/2 \ d[Ni(L)^{3+}]/dt = k[Ni(L)^{2+}][S_2O_8^{2-}]$, oxidation rate constants were determined.

Keywords. Kinetics; oxidation; peroxydisulphate; Ni(II) hexaazamacrocycle; Ni(II) pentaaza macrocycle.

1. Introduction

The chemical behaviour of transition-metal complexes often depends on their redox properties. This is true to a large extent for the natural and synthetic complexes involving macrocyclic ligands such as Ni(II) hexaaza and pentaaza macrocyclic derivatives which are known to display properties and reactivity very close to those of the cyclam analogue and have been documented in literature [1]. Encircling a Ni(II) centre by the 14-membered tetramine macrocycle cyclam allows access to the otherwise unstable Ni(III) and Ni(I) oxidation states. Interestingly both trivalent and monovalent species have been shown to display unusual reactivity. In particular (i) Ni(III) complexes of cyclam and cyclam-like ligands play a catalytic role in DNA modification under oxidative conditions [2] and in the homogeneous oxidation of cyclohexene and arylalkenes to epoxides [3] and (ii) the Ni(I) complexes of cyclam has been proved to mediate the electrochemical reduction of CO_2 [4–8] and alkyl halides [9,10]. Any modification of the 14 membered framework (variation of ring size, introduction of alkyl substituents, introduction of variable degrees of unsaturation etc.) drastically reduces the catalytic efficiency in both processes of types (i) and (ii).

Almost all Ni(II) macrocyclic complexes investigated so far, display the typical macrocyclic inertness towards demetallation by strong acids [11]. Most of the Ni(II) complexes have been isolated as perchlorate salts by the addition of concentrated perchloric acid to the reaction solution. These salts are water soluble and show an extreme kinetic stability, in complete analogy with that found with the corresponding cyclam complexes.

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Xu and McAuley have used $S_2O_8^{2-}$ preparatively to oxidize macrobicyclic Ni(II) complexes but found the kinetics intractable due to side reactions of the SO_4^- radicals [12]. Kinetics and mechanism of oxidation of Ni(II) tetraazamacrocycles by $S_2O_8^{2-}$ anion in aqueous and binary aqueous mixtures have been reported [12] and a similar report on *bis*(1,4,7-triazacyclononane) Ni(II) is found in literature [13,14]. $S_2O_8^{2-}$ has been used to prepare aqueous solutions of Ni(III) polyaza macrocycles [15]. A pulse radiolytic study of the oxidation of Ni(II) complex with an unsaturated macrocyclic ligand by Br_2^- and OH^- radicals in aqueous solutions [16] has been reported. Many kinetic studies have shown the Ni(II) complex to be smoothly oxidized to the +3 state by a variety of oxidants via an outer-sphere mechanism [17].

Since any modification in the framework of macrocycles such as variation of ring size, introduction of alkyl substituents, unsaturation etc. have been shown to affect the redox properties of macrocycles, different types of macrocycles such as hexaaza (polycyclic and monocyclic) and pentaaza (dienes and CH_3-substituted dienes) are chosen for our present work. The kinetics of oxidation of two Ni(II) hexaaza and two Ni(II) pentaaza macrocycles, $[Ni(II)L]^{2+}$, by $S_2O_8^{2-}$ have been studied as a function of $S_2O_8^{2-}$ and pH and are reported in this paper.

2. Experimental

2.1 *Materials*

The Ni(II)L^1 [(L^1 = 1,3,6,9,11,14-hexaazatricyclo(12,2,1,1)) octadecane] perchlorate complex was prepared by a reported procedure [18,19]. Complexes Ni(II) L^2, Ni(II)L^3 and Ni(II) L^4 were also synthesised as perchlorates, vide the procedure reported in the literature [20]. AnalaR grade sodium peroxydisulphate (CDH) was used as such. Lithium perchlorate was prepared by neutralization of lithium carbonate (AR) with $HClO_4$ and was recrystallized from water. All other reagents and solvents were of AnalaR Grade and were used without further purification. All solutions were prepared using doubly distilled deionised water.
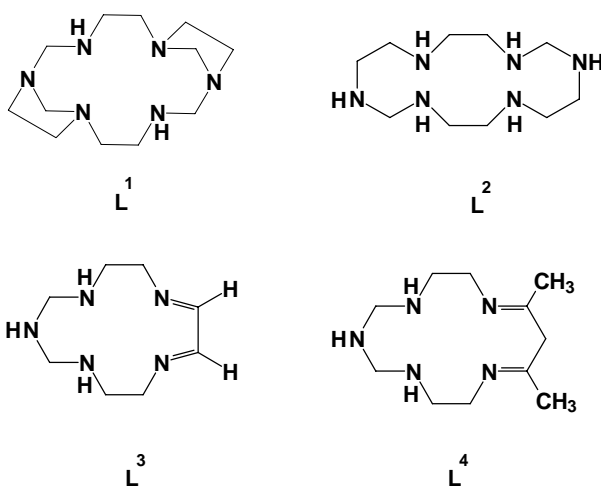
2.2 *Structures of ligands L^1–L^4*

The structures of ligands used in this work are as below:

L^1 = 1,3,6,9,11,14-hexaazatricyclo (12,2,1,1,)octadecane,
L^2 = 1,3,6,9,11,14-hexaazacyclohexadecane,
L^3 = 1,4,6,8,11-pentaazacyclotrideca 11,13-diene,
L^4 = 12,14-dimethyl,1,4,6,8,11-pentaazacyclotetradeca-11,14-diene.

3. Kinetics

Kinetic studies were performed under pseudo-first-order conditions using an excess of peroxydisulphate. Concentrations of the Ni(II) complexes used in this experiment were in the range 2–5×10^{-3} mol dm^{-3}. Changes in absorbance over time were measured using a C-160 MK II spectrophotometer (AIMIL). A constant perchloric acid concentration of 0.01 mol dm^{-3} was maintained to help stabilize the Ni(III) products. Stabilization of Ni(III) complexes in acidic media, as well as in the presence of coordinating ligands, is well-known from kinetic studies [21,22]. Decomposition of the tervalent species at low acidity has been attributed to intramolecular electron transfer involving Ni(II) ligand radical species. Ionic strength was maintained at 0.5 mol dm^{-3} for all kinetic runs, using lithium perchlorate. Absorbance measurements were made at wavelengths chosen between 360 and 450 nm.

4. Results and discussion

The ESR spectrum of the product confirms the formation of Ni(III) species (figure 1). In kinetic studies using UV-Vis spectral changes, an initial rapid decrease in the absorbance was observed followed by a slower decrease. For all the complexes under investigation, plots of log (D_t–D_∞) versus time show two slopes corresponding to an initial fast reaction and a subsequent slow reaction. Rate constants for the second stage of the kinetics are determined from the plot of log (D_t–D_∞) vs time. To determine the rate constants for the initial faster reaction [26], the linear portions corresponding to the slower reactions are extrapolated to zero time, and subtracted point by point from (D_t–D_∞). The logarithm of this difference (D_t–D_c), where D_c is the corresponding absorbance in the extrapolated
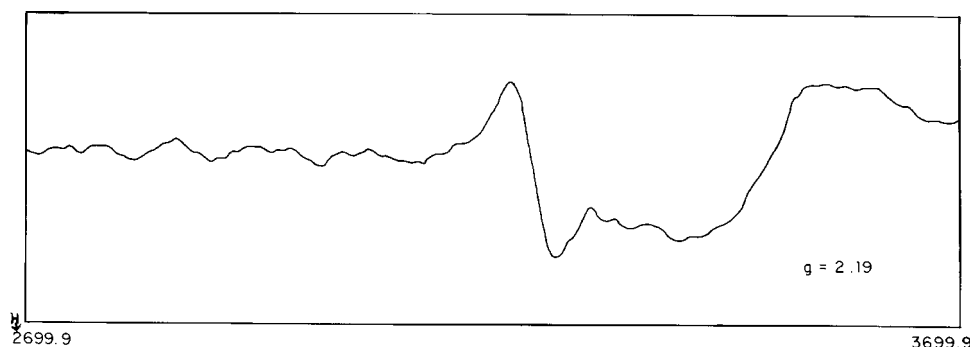

Figure 1. ESR spectrum of the reaction product of NiL^2–Na$_2$S$_2$O$_8$ system.

line, when plotted against time, gives a linear plot from which the rate constant for the initial stage is determined. Rates are almost independent of pH especially in the range $2 < p$H < 4.

An important feature of Ni(II) macrocycles is the coexistence in solution of the high spin and low spin form, according to the interconversion equilibrium

$$[NiLS_2]^{2+} \quad \rightleftharpoons \quad [NiL]^{2+} + 2S,$$
octahedral   square planar
high spin   low spin
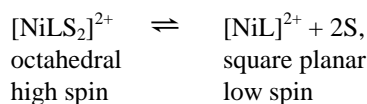
where L is the macrocycle and S, any solvent molecule displaying donor properties[23,24]. In the solvents used, viz. water, and aqueous acetonitrile and DMF, all the reported macrocyclic complexes exist as mixtures of the two forms. This is illustrated by the presence of an absorption band centred at 450 nm (pertinent to the yellow, low spin chromophore) and two absorption bands centred at 330 nm and 530 nm (corresponding to the blue-violet, high spin chromophore) in the UV-Vis spectrum[25] (200–800 nm range). A visible colour change from yellow to purple was observed initially, immediately on the addition of $Na_2S_2O_8$. Initial rapid decrease in the absorbance might be due to two simultaneous reaction, (i) the high spin form reacting with the oxidant, (ii) the high spin form is transformed into the more stable low spin form subsequent slower decrease in the absorbance possibly due to the reaction of the more stable low spin form with $S_2O_8^{2-}$. This is illustrated from the diode-array spectra (figure 2). The overall reaction may be described as,
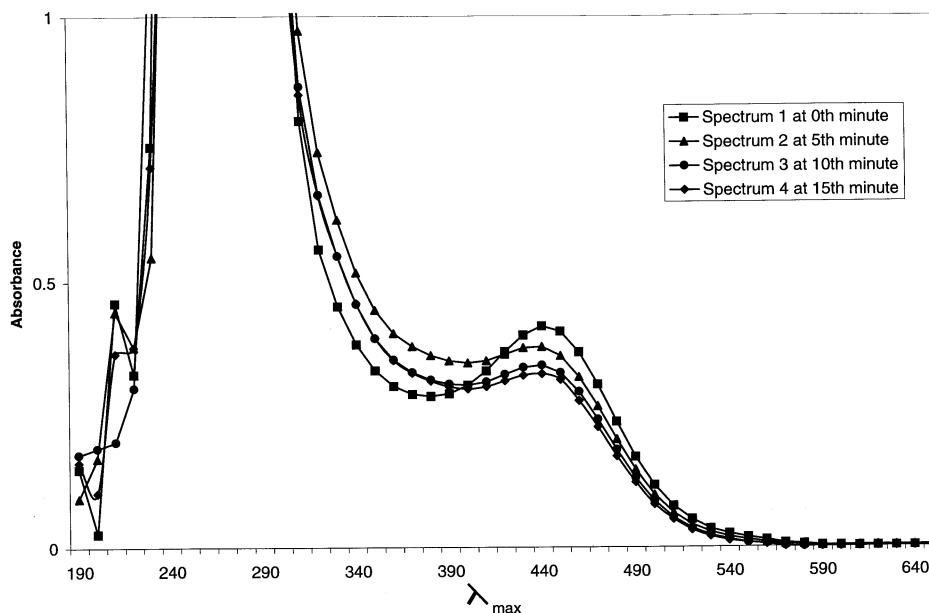
$$2[Ni(II)L]^{2+} + S_2O_8^{2-} \rightarrow 2[Ni(III) L(SO_4)]^+. \tag{1}$$

Figure 2.   Diode-array spectra of NiL^2–Na$_2$S$_2$O$_8$ system at pH = 2 (HClO$_4$).

First-order kinetics is observed for the appearance of Ni(III) products, in all the solvents studied. If SO_4^- radicals were involved in the rate-determining step during the reaction, deviation from first-order behaviour in oxidation of peroxydisulphate would have occurred [27].
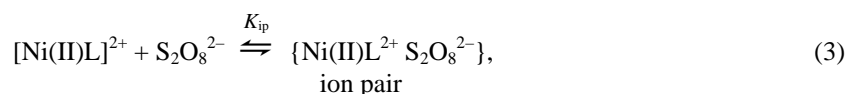
Thus the rate law,

$$\text{rate} = +\tfrac{1}{2}\, d[\text{Ni(III)L}]/dt = k_{\text{obs}}\,[\text{Ni(II)L}], \tag{2}$$

is obeyed.

Table 1 lists the observed first-order rate constants for the oxidation of all the four Ni(II) complexes, studied in aqueous medium, as a function of $S_2O_8^{2-}$ concentration. Rates are almost independent of acid between pH 4 and 2 (table 2), indicating the absence of protonation of the oxidant in this range. This observation is consistent with the reported lack of H-ion dependence [28] in the oxidation of iron(II) by $S_2O_8^{2-}$ up to an acid concentration of 0.01 mol dm^{-3}. The addition of a radical scavenger, allyl acetate [29], caused no change in rates, within experimental error. This suggests that the rate-determining step does not involve the SO_4^- species.

A common mechanism (ignoring, for the moment, interchange between possible inner sphere solvent at the Ni(II) complex and peroxy disulphate) may be described schematically as [30],

$$[\text{Ni(II)L}]^{2+} + S_2O_8^{2-} \underset{}{\overset{K_{\text{ip}}}{\rightleftharpoons}} \{\text{Ni(II)L}^{2+}\, S_2O_8^{2-}\}, \tag{3}$$
$$\text{ion pair}$$

$$\{\text{Ni(II)L}^{2+}\, S_2O_8^{2-}\} \xrightarrow{k_4} [\text{Ni(III)L(SO}_4)]^+ + SO_4^-, \tag{4}$$

$$[\text{Ni(II)L}]^{2+} + SO_4^- \xrightarrow{\text{fast}} [\text{Ni(III)L(SO}_4)]^+. \tag{5}$$

The rate law derived from this scheme is

$$\text{Rate} = 2k_4\, K_{\text{ip}}\, [S_2O_8^{2-}]\, [\text{Ni(II)L}]_{\text{tot}}/(1 + K_{\text{ip}}\, [S_2O_8^{2-}]). \tag{6}$$

Such a rate law is expected to show curvature in the plot of dependence of the observed first order rate constant on $[S_2O_8^{2-}]$, if the ion pairing constant is sufficiently large. In the present system no curvature is seen in the k_{obs} vs $1/[S_2O_8^{2-}]$ plots. This suggests that the ion-pairing constant is small and the approximation,

$$1 + K_{\text{ip}}\, [S_2O_8^{2-}] = 1,$$

is valid over the range of oxidant concentrations used. Hence the rate law is simplified to

$$\begin{aligned}
\text{rate} &= k_{\text{obs}}\, [\text{NiL}^{2+}] \\
&= 2k_4\, K_{\text{ip}}\, [S_2O_8^{2-}].[\text{NiL}^{2+}].
\end{aligned}$$

Table 1. Observed first-order rate constants, k_{obs} (s⁻¹) for the oxidation of Ni(II) macrocyclic complexes as a function of $[S_2O_8^{2-}]$ in aqueous media.

Temp: 26°C; pH = 2 (HClO₄); I = 0·5 mol dm⁻³ (LiClO₄)

[NiL¹] = 5 × 10⁻³ (mol dm⁻³)			[NiL²] = 5 × 10⁻³ (mol dm⁻³)			[NiL³] = 2·5 × 10⁻³ (mol dm⁻³)			[NiL⁴] = 2 × 10⁻³ (mol dm⁻³)		
$[S_2O_8^{2-}]$ (mol dm⁻³)	$k_{obs} \times 10^4$ (s⁻¹)	$*k_1^1 \times 10^4$ (s⁻¹)	$[S_2O_8^{2-}]$ (mol dm⁻³)	$k_{obs} \times 10^4$ (s⁻¹)	$k_1^{1*} \times 10^4$ (s⁻¹)	$[S_2O_8^{2-}]$ (mol dm⁻³)	$k_{obs} \times 10^4$ (s⁻¹)	$k_1^{1*} \times 10^4$ (s⁻¹)	$[S_2O_8^{2-}]$ (mol dm⁻³)	$k_{obs} \times 10^4$ (s⁻¹)	$k_1^{1*} \times 10^4$ (s⁻¹)
0·050	1·09	3·59	0·050	1·42	4·53	0·025	2·88	–	0·02	1·27	–
0·075	1·60	5·21	0·075	1·83	6·62	0·0375	4·61	–	0·03	1·74	–
0·0875	1·88	6·91	0·0875	2·32	6·84	0·050	7·00	–	0·04	2·31	–
0·100	1·96	7·56	0·100	2·61	6·85	0·0625	7·78	1·08	0·05	3·71	–
0·125	2·58	7·59	0·125	3·04	11·7	0·075	8·79	1·20	0·06	4·95	–

$*k_1^1$ = rate constants of initial fast reactions

Table 2. Observed first-order rate constants, k_{obs} (s⁻¹), for the oxidation of Ni(II) macrocyclic complexes under various pH* conditions.

Temp. = 26°C; I = 0·5 mol dm⁻³ (LiClO₄)

pH	[NiL¹] = 5 × 10⁻³ (mol dm⁻³) [S₂O₈²⁻] = 5 × 10⁻² (mol dm⁻³)		[NiL²] = 5 × 10⁻³ (mol dm⁻³) [S₂O₈²⁻] = 5 × 10⁻² (mol dm⁻³)		[NiL³] = 2·5 × 10⁻³ (mol dm⁻³) [S₂O₈²⁻] = 2·5 × 10⁻² (mol dm⁻³)		[NiL⁴] = 2·0 × 10⁻³ (mol dm⁻³) [S₂O₈²⁻] = 6·0 × 10⁻² (mol dm⁻³)	
	$k_{obs} \times 10^4$ (s⁻¹)	$k' \times 10^3$ (s⁻¹)	$k_{obs} \times 10^4$ (s⁻¹)	$k' \times 10^3$ (s⁻¹)	$k_{obs} \times 10^4$ (s⁻¹)	$k' \times 10^3$ (s⁻¹)	$k_{obs} \times 10^4$ (s⁻¹)	$k' \times 10^3$ (s⁻¹)
2·0	3·40	1·13	3·17	1·96	9·29	1·74	5·62	1·15
2·5	2·75	1·26	3·35	1·84	8·91	1·55	5·59	0·91
3·7	2·82	–	3·86	0·49	9·51	1·67	5·78	0·97
4·0	3·04	–	3·59	–	8·83	1·49	6·43	0·92
4·6	2·76	–	3·05	–	11·0	1·70	6·07	1·00
5·0	1·39	–	3·00	–	9·91	2·09	5·52	1·15
5·6	0·11	–	–	–	–	–	–	–
6·0	0·41	–	2·95	–	11·9	2·41	3·32	1·15
7·0	1·60	–	3·10	–	11·93	3·18	2·89	0·86
8·0	1·77	–	3·36	–	14·0	3·22	1·92	1·07

*pH 2–5·6 → Acetate buffer used; pH 6–8 → phosphate buffer used

4.1 *pH effects*

The *p*H of the medium was varied from 2 to 8 using acetate buffer (up to *p*H 5·6) and phosphate buffer (above *p*H 5·6). Log (absorbance) vs time plots, at various *p*H values for all the four Ni(II) macrocycles studied, are linear for several half-lives at lower *p*H (*p*H = 2), whereas at higher *p*H values, the linearity did not persist for longer time intervals due to the formation of Ni(II). The rates are almost independent of acid between $2 < pH < 4$ (table 2).

4.2 *Stability of higher oxidation state of nickel*

An appreciable shift in the stability of oxidation state occurs when there is a change in macrocyclic ring size. An increase in ring size promotes the ease of formation of Ni(I), while rendering the oxidation to Ni(III) more difficult. The difference between the [14]-ane N_4 and [16]-ane N_4 complexes amounts to 0·3 volt in terms of reduction potential [31]. The hole size provided by the macrocyclic ligand should probably decide the stability of the various oxidation states of the central metal ion. The greater the hole size the lesser will be the stability of Ni(III). The observed rate constants appear to reflect this for all the four complexes studied. This means that k_{obs} values for NiL^3 and NiL^4 are higher compared to that of NiL^1 and NiL^2 because of the reduction in ring size. In general, reaction Ni(II) $\rightarrow$ Ni(I) is seen to occur with greater ease than Ni(II) $\rightarrow$ Ni(III). The larger Ni(I) cation can be more easily accommodated in a larger 'hole'. The 13- or 14-membered ring (NiL^3 and NiL^4 respectively) provides a considerably stronger ligand field for a coordinated metal ion than does the corresponding 16-membered ring (NiL^1 and NiL^2). Also complexes of [16] N_4 are much less resistant to solution decomposition than the analogous [14] N_4 complexes. Further, increasing the extent of ligand unsaturation results in a stronger ligand field towards the coordinated Ni(II) ion [32–34].

Acknowledgement

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