Kinetics of the Oxidation of Thioglycolic and Thiomalic Acids by a Nickel(III) Oxime–Imine Complex

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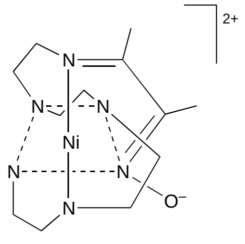
The kinetics of the oxidation of thioglycolic and thiomalic acids by $[Ni^{III}L^1]^{2+}$ (where HL^1 = 15-amino-3-methyl-4,7,10,13-tetraazapentadec-3-en-2-one oxime) have been investigated at 30.0 °C; an inner-sphere mechanism for both the reactions has been proposed except for the fully deprotonated species of thiomalic acid which follows an outer-sphere route.

Studies on the thiol–disulfide interchange reactions are of immense importance in biochemistry.[1,2] However this type of transformation by metal complexes has received much less attention. In this investigation we present the kinetic results on the oxidation of thioglycolic acid (H_2A) and thiomalic acid (H_3A) by the nickel(III) oxime–imine complex **I**.



I

Spectrophotometric determination at 498 nm (λ_{max} for $[Ni^{III}(L^1)]^{2+}$, hereafter designated as Ni^{III}) revealed a 1:1 stoichiometric ratio for both the reactions leading to the disulfide products [eqn. (1)].

$$2Ni^{III} + 2RSH \rightarrow 2Ni^{II} + RSSR + 2H^+ \qquad (1)$$

RSH and RSSR represent respectively the thiols and the corresponding disulfide products. Generation of free radicals and characterisation of disulfide products were achieved by reported[9,24] methods. Under pseudo-first-order conditions with varied concentrations of reductants, a plot of k_{obs} *vs.* $[H_2A]_T$ gives a straight line passing through the origin whereas that for H_3A is a limiting curve of decreasing slope with nearly zero intercept (Table 1). The corresponding rate laws are given by eqns. (2) and (3) respectively.

$$-d/dt[Ni^{III}] = k[H_2A][Ni^{III}] = k_{obs}[Ni^{III}] \qquad (2)$$

$$-d/dt[Ni^{III}] = \frac{kQ[H_3A]_T[Ni^{III}]}{1 + Q[H_3A]_T} = k_{obs}[Ni^{III}] \qquad (3)$$

$$Ni^{III} + H_3A \overset{Q}{\rightleftharpoons} Ni^{III}\cdot H_3A \xrightarrow{k} \text{Products} \qquad (3a)$$

Q is the association constant as defined by eqn. (3a) and represents the oxidation of thiomalic acid.

The effect of acidity on the reaction rates was investigated in the pH range 2.51–8.05 for H_2A and 2.71–8.25 for H_3A as shown in Figs 1(*a*) and (*b*). Dependence on acidity can best be explained by considering the p*K* values of H_2A and H_3A.[25] In the experimental pH range, the existing thioglycolic acid species are H_2A, HA^- and A^{2-}. Their reactions can be portrayed as:

$$Ni^{III} + H_2A \rightarrow Ni^{II} + \text{radical} \qquad (4)$$

$$Ni^{III} + HA^- \rightarrow Ni^{II} + \text{radical} \qquad (5)$$

$$Ni^{III} + A^2 \rightarrow Ni^{II} + \text{radical} \qquad (6)$$

Table 1 Pseudo-first-order rate constants at various reductant concentrations for the oxidations of thioglycolic acid and thiomalic acid by $[Ni^{III}(L^1)]^{2+}$ with $[[Ni^{III}(L^1)]^{2+}] = 5.0 \times 10^{-5}$ mol dm^{-3}, I = 0.2 mol dm^{-3} ($NaClO_4$), $[OAc^-]$ = 0.02 mol dm^{-3} and temperature = 30.0 °C

Reductant	10^2[Reductant]/ mol dm^{-3}	k_{obs}/s^{-1} pH 4.75	k_{obs}/s^{-1} pH 5.90
Thioglycolic acid	0.10	0.10	
	0.30	0.27	
	0.50	0.41	
	0.70	0.56	
	0.90	0.69	
Thiomalic acid	0.05		0.75
	0.10		1.25
	0.20		1.79
	0.30		2.33
	0.50		2.94
	0.70		3.44
	1.00		4.11

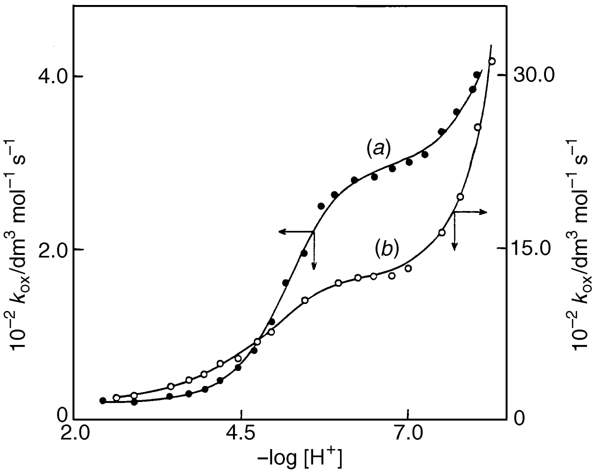


Fig. 1 Variation of k_{ox} as a function $-\log[H^+]$ for the reduction of $[Ni^{III}(L^1)]^{2+}$ by (*a*) thioglycolic acid and (*b*) thiomalic acid at 30.0 °C with $[Ni^{III}(L^1)]^{2+}] = 5.0 \times 10^{-5}$ mol dm^{-3}, I = 0.20 mol dm^{-3} ($NaClO_4$) and [buffer] = 0.02 mol dm^{-3}: the solid line represents calculated values, points represent experimental values

$$\text{radical} + \text{radical} \rightarrow \text{disulfide} \qquad (7)$$

The general rate law derived from the above is:

$$k_{ox} = \frac{k_4[H^+]^2 + k_5K_1[H^+] + k_6K_1}{[H^+]^2 + K_1[H^+] + K_1K_2} \qquad (8)$$

Considering the pH range 2.51–6.70, the parameters k_4, k_5 and K_1 were evaluated by a non-linear least-squares programme: $k_4 = (22.5 \pm 2.8)$ dm^3 mol^{-1} s^{-1}, $k_5 = (3.05 \pm 0.10) \times 10^2$ dm^3 mol^{-1} s^{-1} and $K_1 = (5.36 \pm 0.13)$

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$\times 10^{-6}$ mol dm^{-3} (p$K_1 = 5.23$, reported 3.58). Similarly from the pH range 7.0–8.05, the values of $k_5 = (2.86 \pm 0.1) \times 10^2$ dm^3 mol^{-1} s^{-1} and $k_6 = (5.36 \pm 0.13) \times 10^3$ dm^3 mol^{-1} s^{-1} were obtained using $K_2 = 1.66 \times 10^{-10}$ mol dm^{-3}.

The reacting species of thiomalic acid in the experimental pH range are H_3A, H_2A^-, HA^{2-} and A^{3-}. Their reactions towards the Ni^{III} complex can be represented by:

$$\mathrm{Ni^{III}} + \mathrm{H_3A} \rightarrow \mathrm{Ni^{II}} + \text{radical} \tag{12}$$

$$\mathrm{Ni^{III}} + \mathrm{H_2A^-} \rightarrow \mathrm{Ni^{II}} + \text{radical} \tag{13}$$

$$\mathrm{Ni^{III}} + \mathrm{HA^{2-}} \rightarrow \mathrm{Ni^{II}} + \text{radical} \tag{14}$$

$$\mathrm{Ni^{III}} + \mathrm{A^{3-}} \rightarrow \mathrm{Ni^{II}} + \text{radical} \tag{15}$$

The corresponding rate law is:

$$k_{\mathrm{ox}} = \frac{k_{12}[\mathrm{H}^+]^3 + k_{13}K_1[\mathrm{H}^+]^2 + k_{141}K_2[\mathrm{H}^+] + \mathrm{k}_{15}K_1K_2K_3}{[\mathrm{H}^+]^3 + K_1[\mathrm{H}^+]^2 + K_1K_2[\mathrm{H}^+] + K_1K_2K_3} \tag{16}$$

In suitable pH ranges, the values of the evaluated parameters are: $k_{12} = (1.72 \pm 0.3) \times 10^2$ dm^3 mol^{-1} s^{-1}, $k_{13} = (4.10 \pm 0.2) \times 10^2$ dm^3 mol^{-1} s^{-1}, $k_{14} = (1.24 \pm 0.5) \times 10^3$ dm^3 mol^{-1} s^{-1}, $k_{15} = (2.53 \pm 0.09) \times 10^5$ dm^3 mol^{-1} s^{-1}, $K_1 = (4.15 \pm 0.03) \times 10^{-4}$ mol dm^{-3} (p$K_1 = 3.38$, reported 3.64) and $K_2 = (9.77 \pm 0.05) \times 10^{-6}$ mol dm^{-3} (p$K_2 = 5.01$, reported 4.64). Putting the corresponding evaluated parameters in eqns. (8) and (16), k_{ox} values at different experimental [H$^+$] were obtained and these showed an excellent agreement with the experimental values for both thiols.

The low spin ($t_{2g}^6e_g^1$) nickel(III) complexes having an unpaired electron in the d_{z^2} orbital are generally substitutionally inert, although there is no experimental estimate of the ligand exchange rate for [Ni^{III}(L^1)]$^{2+}$ and thereby reactions involving this complex are likely to follow an outer-sphere route. However, the formation of a hydrogen bonded intermediate in many of the electron transfer reactions of Ni$^{III/IV}$ oxime–imine complexes[17,20–22] has been proposed. The initial rapid increase in the absorbance in the 20–30 ms timescale of thioglycolic acid oxidation points to inner-sphere coordination of the thiol molecule to the metal centre, probably by the partial release of one of the nitrogen atoms of the coordinated N_6-oxime–imine frame. In the oxidation of thiomalic acid and other carboxylic acids (glycolic and malic acid), no such initial rise in absorbance was noted but the former oxidation was found to proceed through rate saturation. The higher reactivity of H_2A towards [Ni^{III}(L^1)]$^{2+}$ ($E° = 0.49$ V, $k_{\mathrm{ex}} = 10^2$ dm^3 mol^{-1} s^{-1}) is higher than that towards [Mn^{III}(cdta)]$^-$ ($E° = 0.81$ V, $k_{\mathrm{ex}} = 4.4 \times 10^8$ dm^3 mol^{-1} s^{-1}). This can be explained by considering the hydrogen bond formation between the carboxylato hydrogen atom and the oximato oxygen atom ($=$N—O$^-$), which may substantially increase the lability of the metal centre through the sulfur atom and thereby provide a lower energy pathway for the electron transfer process. The lack of a carboxylato proton in HA$^-$ and A^{2-} species explains their lower reactivity towards [Ni^{III}(L^1)]$^{2+}$ than [Mn^{III}(cdta)]$^-$. For the oxidation of thiomalic acid, a higher formation constant obtained from kinetics indicates that the reaction proceeds either through the initial formation of a hydrogen bonded adduct or through the coordination of the ligand to the metal centre by the SH group. In the oxidation of A^{3-}, no hydrogen bonding effect is possible and so an outer-sphere mechanism is more likely.

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Techniques used: UV–VIS, elemental analysis, pH-metry

References: 29

Table 2: Pseudo-first-order rate constants at various concentrations of glycolic acid and malic acid

Table 3: Decomposition rate of [Ni^{III}(L^1)]$^{2+}$ as a function of pH at 40.0 °C

Fig. 2: k_{ox} *vs.* $-\log[\mathrm{H}^+]$ for malic acid oxidation by [Ni^{III}(L^1)]$^{2+}$

Schemes: 2

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