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Electron transfer from thiosulfate to nickel(IV) oxime imine complexes in aqueous solution

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The kinetics of oxidation of thiosulfate by the complexes $[\mathrm{Ni^{IV}L^3{}_2}]^{2+}$ and $[\mathrm{Ni^{IV}L^2}]^{2+}$ ($\mathrm{HL^3}$ = 6-amino-3-methyl-4-azahex-3-en-2-one oxime, $\mathrm{H_2L^2}$ = 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime) was studied spectrophotometrically under pseudo-first-order conditions with an excess of thiosulfate in the range pH 2.50–8.0 with $[\mathrm{Ni^{IV}}] = 5.0 \times 10^{-5}$ mol dm^{-3}, $[\mathrm{S_2O_3{}^{2-}}] = (1.0\text{–}10.0) \times 10^{-3}$ mol dm^{-3}, I = 0.20 mol dm^{-3} ($\mathrm{NaClO_4}$) at 20 °C. A monophasic two-electron transfer was found in the regions $3.0 \leqslant \mathrm{pH} \leqslant 5.0$ and $2.5 \leqslant \mathrm{pH} \leqslant 4.0$ for reduction of the two complexes respectively. Above these pH regions both reactions showed biphasic decay with an initial faster step $\mathrm{Ni^{IV}} \longrightarrow \mathrm{Ni^{III}}$ and second slower step $\mathrm{Ni^{III}} \longrightarrow \mathrm{Ni^{II}}$, and the general rate law is $-\mathrm{d}[\mathrm{Ni^{IV}(L}_x)^{2+}]/\mathrm{d}t = k_{\mathrm{obs}}[\mathrm{Ni^{IV}(L}_x)^{2+}] = 2nk[\mathrm{Ni^{IV}(L}_x)^{2+}][\mathrm{S_2O_3{}^{2-}}]$ where $2n$ is a stoichiometric factor. All the kinetic parameters have been evaluated by choosing suitable pH regions. An additional protonation of the nickel(IV) complexes ($\mathrm{p}K_\mathrm{a}$ = 4.91 and 4.28 respectively) has been encountered and a realistic interpretation is achieved by considering a weak acid–base interaction arising out of outer-sphere protonation of the $[\mathrm{Ni^{IV}(L}_x)]^{2+}$ complexes. All the reaction steps have been scrutinised. The reduction $[\mathrm{Ni^{IV}(L}_x)]^{2+} \longrightarrow [\mathrm{Ni^{III}(L}_x)]^+$ is assumed to follow an outer-sphere mechanism whereas $[\mathrm{Ni^{III}(L}_x)]^+ \longrightarrow [\mathrm{Ni^{II}(L}_x)]$ follows an inner-sphere route. The calculated electron-transfer rate constant (k_{12}) obtained through Marcus cross-reaction relations can be considered as a proof of such delineation.

Concerted electron and proton-transfer reactions are of vital importance in chemistry and biochemistry.[1] Of particular interest is the case in which a transition-metal ion is bound to ligand sites having dissociable protons. This occurs with a *few* nickel-(IV) and -(III) complexes with oxime–imine ligands *e.g.* **I**–**III** and the redox potentials are greatly influenced by the acidity of the medium.[2] Electrochemical studies on $[\mathrm{Ni^{IV}L^3{}_2}]^{2+}$ and $[\mathrm{Ni^{IV}L^2}]^{2+}$ reveal at low pH a single-step two-electron transfer and at high pH two separate one-electron reductions.[2–4] The nickel-(IV) to -(III) step [equation (1)] is independent of pH ($\mathrm{p}K_\mathrm{h} < 1.0$) whereas the reduction of nickel(III) [equations (3) and (4)] is pH dependent arising from the proton equilibrium[3,4] [equation (2)]. These redox potentials[2] are useful in mechanistic delineation of the chemical reactions of these complexes. Although there have been a couple of studies of such reactions, much remains to be learned regarding the reduction by sulfur oxyanions. Thiosulfate is one of the most important industrial and biological molecules. It is also much used as an analytical reagent. Unlike sulfate, thiosulfate possesses an extensive redox chemistry. Depending upon the nature and potential, it results in a zero-[5,6] or first-order[7–11] dependence of the rate on the oxidant concentration. The present investigation is concerned with the kinetics of reactions of thiosulfate with $[\mathrm{Ni^{IV}L^3{}_2}]^{2+}$ and $[\mathrm{Ni^{IV}L^2}]^{2+}$. The general features of the intrinsic mechanism are discussed in relation to Marcus cross-reaction parameters.

$$[\mathrm{Ni^{IV}(L}_x)]^{2+} + \mathrm{e}^- \rightleftharpoons [\mathrm{Ni^{III}(L}_x)]^+ \qquad (1)$$

$$E^\circ[\mathrm{Ni^{IV}L^3{}_2{}^{2+/+}}] = 0.63,\ E^\circ[\mathrm{Ni^{IV}(L^2)^{2+/+}}] = 0.654\ \mathrm{V}\ (vs.\ \mathrm{NHE})$$

$$[\mathrm{Ni^{III}(HL}_x)]^{2+} \xrightleftharpoons{K'_\mathrm{h}} [\mathrm{Ni^{III}(L}_x)]^+ + \mathrm{H}^+ \qquad (2)$$

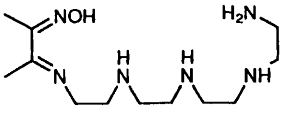
$$\mathrm{p}K'_\mathrm{h}\ [\mathrm{Ni^{III}L^3(HL^3)}]^{2+} = 4.43,\ \mathrm{p}K'_\mathrm{h}\ [\mathrm{Ni^{III}(HL^2)}]^{2+} = 4.03$$

$$[\mathrm{Ni^{III}(HL}_x)]^{2+} + \mathrm{e}^- \rightleftharpoons [\mathrm{Ni^{II}(HL}_x)]^+ \qquad (3)$$

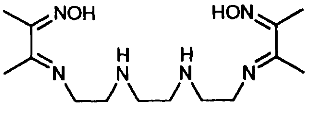
$$E^\circ[\mathrm{Ni^{III}(L^3)(HL^3)^{2+/+}}] = 0.63,\ E^\circ[\mathrm{Ni^{III}(HL^2)^{2+/+}}] = 0.640\ \mathrm{V}$$

$$[\mathrm{Ni^{III}(L}_x)]^+ + \mathrm{e}^- \rightleftharpoons [\mathrm{Ni^{II}(L}_x)] \qquad (4)$$

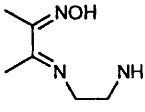
$$E^\circ[\mathrm{Ni^{III}L^3{}_2{}^{+/0}}] = 0.30,\ E^\circ[\mathrm{Ni^{III}(L^2)^{+/0}}] = 0.42\ \mathrm{V}$$



$\mathrm{HL^1}$
I



$\mathrm{H_2L^2}$
II



$\mathrm{HL^3}$
III

Experimental

Kinetics and other measurements

A Shimadzu UV/VIS, recording spectrophotometer (UV 2100) equipped with thermostatted cell compartments was used for the kinetic measurements. The disappearance of the oxidants was monitored at 505 and 500 nm for $[\mathrm{NiL^3{}_2}]^{2+}$ and $[\mathrm{NiL^2}]^{2+}$ respectively at various pH, keeping the ionic strength (0.2 mol dm^{-3}) and temperature (20 ± 0.1 °C) constant throughout as discussed earlier.[12]

Materials and reagents

The nickel-(II) and -(IV) complexes of $\mathrm{HL^3}$ and $\mathrm{H_2L^2}$ {hereafter designated as $[\mathrm{Ni^{II/IV}(L}_x)]$ in general unless mentioned specifically} were prepared and characterised by the literature methods.[2] Analytical reagent-grade sodium thiosulfate (Fluka AG) was used without further purification. All the thiosulfate solutions were prepared freshly and standardised with standard dichromate solution. Sodium perchlorate, sodium acetate–acetic acid and sodium dihydrogenphosphate–sodium hydroxide (all reagent grade) were used to maintain the ionic strength and pH of the solution. The sodium salts were recrystallised twice before use. All solutions were prepared freshly using doubly distilled water which had been prepared in an all-glass still.

Stoichiometry and reaction product

The stoichiometry of the reactions between the nickel(IV) complexes and thiosulfate in aqueous solution at a particular pH and ionic strength was investigated by monitoring the change in absorbance maximum of the nickel(IV) complexes. With initial concentrations of $[\mathrm{Ni^{IV}}(\mathrm{L}_x)^{2+}] = 1.0 \times 10^{-4}$ mol dm^{-3} and $[\mathrm{S_2O_3}^{2-}] = 2 \times 10^{-4}$ mol dm^{-3} complete consumption of Ni$^{\mathrm{IV}}$ was noted. Increasing the concentration of Ni$^{\mathrm{IV}}$ from 2×10^{-4} to 1×10^{-3} mol dm^{-3} and keeping $[\mathrm{S_2O_3}^{2-}] = 2 \times 10^{-4}$ mol dm^{-3} at pH 4.50, the consumption ratio of $[\mathrm{Ni^{IV}}]:[\mathrm{S_2O_3}^{2-}]$ varied from 1:1.7 to 1:1. These results indicate that under the actual reaction condition, *i.e.* with a variable excess of $[\mathrm{S_2O_3}]^{2-}$ and a fixed concentration of $[\mathrm{Ni^{IV}}(\mathrm{L}_x)]^{2+}$, the consumption ratio of nickel(IV) to $\mathrm{S_2O_3}^{2-}$ would assume a limiting value of 1:2. The determination of the reaction stoichiometry at $[\mathrm{S_2O_3}^{2-}]:[\mathrm{Ni^{IV}}] \geqslant 10:1$ by titration of unreacted thiosulfate with iodine was not successful. Under our reaction conditions the sulfur-containing product was determined as tetrathionate according to a reported procedure.[13] When the final solution is allowed to stand at room temperature for *ca.* 24 h after completion of reaction, the tetrathionate is hydrolysed to sulfate.[14] However, this makes a negligible contribution to the overall kinetics.

Thus the stoichiometry would in general be given by equation (5) for the two-electron transfer and by (6) for the one-electron transfer.

$$[\mathrm{Ni^{IV}}(\mathrm{L}_x)]^{2+} + 2\mathrm{S_2O_3}^{2-} \longrightarrow [\mathrm{Ni^{II}}(\mathrm{L}_x)] + \mathrm{S_4O_6}^{2-} \quad (5)$$

$$2[\mathrm{Ni^{IV/III}}(\mathrm{L}_x)]^{2+/+} + 2\mathrm{S_2O_3}^{2-} \longrightarrow 2[\mathrm{Ni^{III/II}}(\mathrm{L}_x)]^{+/0} + \mathrm{S_4O_6}^{2-} \quad (6)$$

Results

The kinetic studies were performed under pseudo-first-order conditions with an excess of thiosulfate over Ni$^{\mathrm{IV}}$. A typical spectral scanning showed no indication of the formation of appreciable amounts of thermodynamically stable intermediates. A single-step two-electron transfer process was found in the region $3.0 \geqslant \mathrm{pH} \geqslant 5.0$ for $[\mathrm{Ni^{IV}L^3}_2]^{2+}$ and $2.5 \leqslant \mathrm{pH} \leqslant 4.0$ for $[\mathrm{Ni^{IV}L^2}]^{2+}$ reduction. A distinct biphasic one-electron transfer reaction appeared at pH $\geqslant$ 6.0 and $\geqslant$ 5.0 for the respective complexes. In these the initial faster step corresponds to the conversion $\mathrm{Ni^{IV}} \longrightarrow \mathrm{Ni^{III}}$ and the relatively slower decay to $\mathrm{Ni^{III}} \longrightarrow \mathrm{Ni^{II}}$. Since $\mathrm{p}K_\mathrm{h} < 1.0$ for both nickel(IV) complexes,[3,4] the couples $[\mathrm{NiL^3}_2]^{2+/+}$ and $[\mathrm{NiL^2}]^{2+/+}$ are expected to exist throughout the region pH 2.50–8.0 and have $E^\circ = 0.63$ and 0.654 V,[2] respectively, in this range.

At lower pH the $\mathrm{Ni^{IV}} \longrightarrow \mathrm{Ni^{III}}$ conversion is rate determining and is followed by very fast reduction of Ni$^{\mathrm{III}}$ to Ni$^{\mathrm{II}}$ (see below) resulting in an overall single-step two-electron transfer. At higher pH $E^\circ(\mathrm{Ni^{IV/III}}) > E^\circ(\mathrm{Ni^{III/II}})$ for the deprotonated nickel(III) and the pK_h values are such (see above) that $[\mathrm{Ni^{III}}(\mathrm{L}_x)]^+$ is the predominant reactive species resulting in a lowering of the reduction potential and consequent separation into two reaction phases.

Semilogarithmic plots for the disappearance of nickel(IV) species in the single-step electron-transfer process were linear up to 70% completion of the total reaction [Fig. 1(*a*)]. From the slopes of such plots the pseudo-first-order rate constants (k_obs) were calculated. For the two consecutive steps [Fig. 1(*b*)] the absorbance *vs.* time curves were successfully treated in terms of two first-order reactions and values of $k_{1(\mathrm{obs})}$ and $k_{2(\mathrm{obs})}$ were obtained from the initial and final slopes (clearly distinct) of plots of $-\log(A_t - A_\infty)$ *vs.* *t*.

Test for catalytic effect of copper(II) impurity

As in many oxidation reactions of thiosulfate,[15] the addition of copper(II) ion to the reaction mixture was found to catalyse the observed rate, but to obey saturation kinetics at $[\mathrm{Cu^{2+}}] = 2.0 \times 10^{-4}$ mol dm^{-3}. For example, the pseudo-first-order rate constant k_obs increased from 12.9×10^{-3} to 34.7×10^{-3} s^{-1} on addition of 2.0×10^{-4} mol dm^{-3} copper(II) ion with $[\mathrm{S_2O_3}^{2-}] = 2.0 \times 10^{-3}$ mol dm^{-3}, $[\mathrm{Ni^{IV}L^3}_2{}^{2+}] = 5.0 \times 10^{-5}$ mol dm^{-3}, $I = 0.20$ mol dm^{-3} and pH 4.50. Addition of 1.0×10^{-3} mol dm^{-3} sodium oxalate or 1.0×10^{-4} mol dm^{-3} $\mathrm{Na_2H_2edta}$ (edta = ethylenediaminetetraacetate) to the reaction mixture containing copper(II) ion nullified this catalytic effect. However, the above k_obs values did not vary on adding the same amount of sodium oxalate or $\mathrm{Na_2H_2edta}$ in the absence of copper(II) ion. This observation indicates the absence of any trace metal-ion impurity in the present system.

Dependence on $[\mathrm{S_2O_3}^{2-}]$

The dependence of the observed rates (k_obs) on reductant concentration was investigated at pH 4.0 and 6.50 for $[\mathrm{Ni^{IV}L^3}_2]^{2+}$ and at pH 3.0 and 5.75 for $[\mathrm{Ni^{IV}L^2}]^{2+}$. Conditions: $[\mathrm{S_2O_3}^{2-}]_\mathrm{T} = (1.0\text{–}10.0) \times 10^{-3}$ mol dm^{-3}, $[\mathrm{Ni^{IV}}(\mathrm{L}_x)^{2+}] = 5.0 \times 10^{-5}$ mol dm^{-3}, $I = 0.20$ mol dm^{-3} ($\mathrm{NaClO_4}$), 20 °C. Plots of k_obs *vs.* $[\mathrm{S_2O_3}^{2-}]_\mathrm{T}$ at all pH were linear passing through the origin, indicating a first-order dependence of rate on thiosulfate concentration and the rate law (7) where *n* is the stoichiometric factor with respect to the

$$-\mathrm{d}[\mathrm{Ni^{IV}}(\mathrm{L}_x)^{2+}]/\mathrm{d}t = k_\mathrm{obs}[\mathrm{Ni^{IV}}(\mathrm{L}_x)^{2+}] = 2nk[\mathrm{S_2O_3}^{2-}][\mathrm{Ni^{IV}}(\mathrm{L}_x)^{2+}] \quad (7)$$

oxidant having the value 0.50 for the two-electron transfer and 1 for the one-electron transfer. The results are summarised in Table 1.

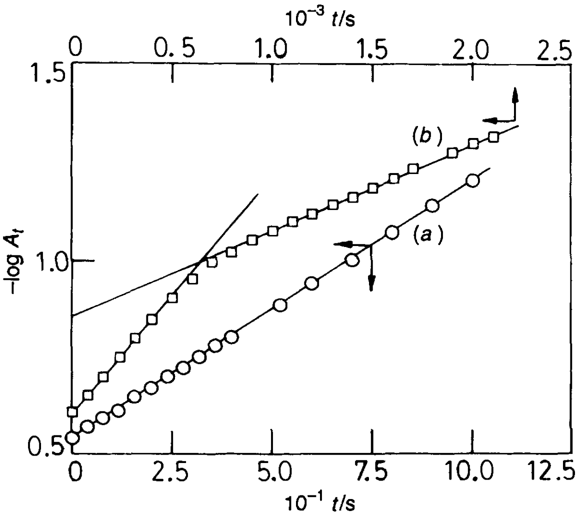


Fig. 1 Plots of $-\log A_t$ *vs.* *t* for the reduction of $[\mathrm{Ni^{IV}L^3}_2]^{2+}$ by thiosulfate. Conditions: $[\mathrm{Ni^{IV}}] = 5 \times 10^{-5}$ mol dm^{-3}, $[\mathrm{S_2O_3}^{2-}] = 2 \times 10^{-3}$ mol dm^{-3}, $I = 0.20$ mol dm^{-3} ($\mathrm{NaClO_4}$) and 20 °C pH (*a*) 4.00 (acetate buffer, 0.02 mol dm^{-3}), (*b*) 7.00 (disodium hydrogenphosphate buffer, 0.02 mol dm^{-3})

Table 1 Pseudo-first-order rate constants for the oxidation of thiosulfate by $[Ni^{IV}L^3{}_2]^{2+}$ and $[Ni^{IV}L^2]^{2+}$ at different pH at 20 °C, I = 0.20 mol dm^{-3} ($NaClO_4$), $[Ni^{IV}]$ = 5.0 × 10^{-5} mol dm^{-3}, [buffer] = 0.02 mol dm^{-3} (phosphate or acetate)

		$10^3k_{obs}/s^{-1}$				
Oxidant	$10[S_2O_3{}^{2-}]$/ mol dm^{-3}	pH 3.0	pH 4.0	pH 5.75	pH 6.50	
$[Ni^{IV}L^3{}_2]^{2+}$	0.01		13.3		1.13^a	0.49^b
	0.02		15.1		2.04^a	0.87^b
	0.03		26.2		2.95^a	1.28^b
	0.045		39.3		—	—
	0.05		45.4		5.05^a	2.14^b
	0.07		59.6		6.85^a	3.15^b
	0.10		80.5		—	—
$[Ni^{IV}L^2]^{2+}$	0.01	5.3				
	0.02	10.7		0.92^a	0.24^b	
	0.03	16.0		1.13^a	0.33^b	
	0.04	22.0		1.44^a	0.47^b	
	0.06	30.2		2.35^a	0.61^b	
	0.08			2.93^a	0.81^b	

^{a} For $Ni^{IV} \longrightarrow Ni^{III}$. ^{b} For $Ni^{III} \longrightarrow Ni^{II}$.

Dependences on $[H^+]$ and $[Ni^{II}]$

The reaction rates were found to be influenced by the acidity of the medium (pH 3.0–8.0 for $[Ni^{IV}L^3{}_2]^{2+}$ and 2.50–7.0 for $[Ni^{IV}L^2]^{2+}$) at $[S_2O_3{}^{2-}]$ = 2.0 × 10^{-3} mol dm^{-3}, and the results are depicted in Figs. 2 and 3. No significant change in the observed rate constants (k_{obs}) was observed on initial addition of nickel(II) complexes to the reaction mixtures.

Discussion

Based on the poor substitution lability of the nickel-(IV) and -(III) complexes a general outer-sphere mechanism, consistent with the kinetic observations, can be expressed as in Scheme 1.

$$Ox + S_2O_3{}^{2-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Red + S_2O_3{}^{-} \qquad (8)$$

$$S_2O_3{}^{-} + S_2O_3{}^{2-} \overset{K_{rad}}{\rightleftharpoons} S_4O_6{}^{3-} \qquad (9)$$

$$Ox + S_4O_6{}^{3-} \xrightarrow{k_3} Red + S_4O_6{}^{2-} \qquad (10)$$

Scheme 1

The existence of the proposed intermediates, aqueous thiosulfate and tetrathionate radicals, is well supported in the literature.[15,16] The decay of $S_2O_3{}^-$ by reactions such as (11)

$$2S_2O_3{}^{-} \longrightarrow S_4O_6{}^{2-} \qquad (11)$$

can be ignored for two reasons: (*i*) such a mechanism would involve a second-order decay of the intermediate resulting in a relatively high steady-state concentration of it; (*ii*) the equilibrium constant K_{rad} is known[15] and under our experimental conditions the equilibrium would be established rapidly relative to the k_2 step which would lead to comparable concentrations of the two radicals. The $E°$ for $S_4O_6{}^{2-/3-}$ has been estimated to be −1.08 V.[15] Thus reaction (10) is expected to have a huge driving force leading to very fast disappearence of the $S_4O_6{}^{3-}$ radical. Thus it is apparent that this step would provide a much more efficient pathway for decay of the radical intermediate than would self-association. There is no kinetic evidence that the reverse electron-transfer reaction (k_2) occurs to a significant extent as no kinetic inhibition upon addition of nickel(II) complexes, the reduction products, was observed. It is thus reasonable to apply the steady-state approximation to the radicals, leading to the rate law (12) where n denotes the stoichiometry factor as discussed earlier; considering that $k_2[Red] \ll K_{rad}k_3[S_2O_3{}^{2-}][Ox]$, the rate law simplifies to (13) which conforms to our experimental observations.

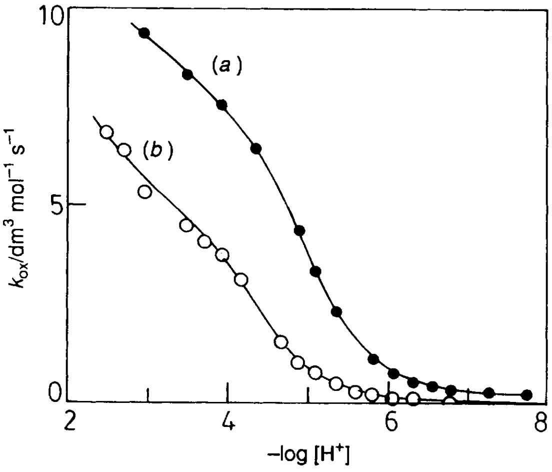


Fig. 2 Plot of k_{ox} *vs.* $-\log[H^+]$ for the reduction of nickel-(IV) to -(III) by thiosulfate at I = 0.20 mol dm^{-3}, $[Ni^{IV}]$ = 5.0 × 10^{-5} mol dm^{-3}, $[S_2O_3{}^{2-}]_T$ = 2.0 × 10^{-3} mol dm^{-3}, 20 °C; (*a*) $[Ni^{IV}L^3{}_2]^{2+}$, (*b*) $[Ni^{IV}L^2]^{2+}$. The solid lines represent calculated and the points the experimental values

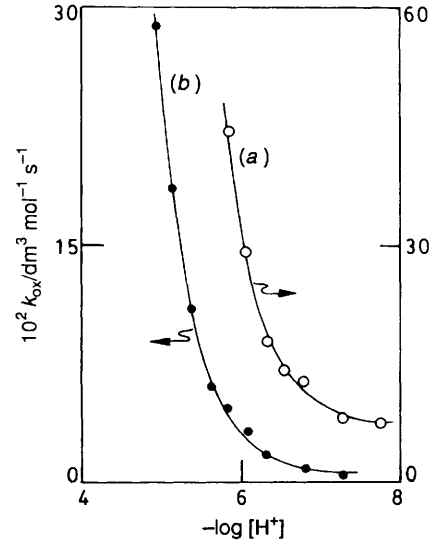


Fig. 3 Plot of k_{ox} *vs.* $-\log[H^+]$ for the reduction of (*a*) Ni^{III}–L^3 and (*b*) Ni^{III}–L^2 by thiosulfate; other details as Fig. 2

$$\frac{-\mathrm{d}[\mathrm{Ox}]}{\mathrm{d}t} = \frac{2nk_1k_3K_{\mathrm{rad}}[\mathrm{Ox}]^2[\mathrm{S_2O_3}^{2-}]^2}{k_2[\mathrm{Red}] + k_{\mathrm{rad}}k_3[\mathrm{S_2O_3}^{2-}][\mathrm{Ox}]} \qquad (12)$$

$$-\mathrm{d}[\mathrm{Ox}]/\mathrm{d}t = 2nk_1[\mathrm{Ox}][\mathrm{S_2O_3}^{2-}] \qquad (13)$$

Reduction of nickel(IV)

The pH *vs.* rate profile for the thiosulfate reduction of $[\mathrm{Ni^{IV}(L_x)}]^{2+}$ reveals some interesting aspects. A plot of k_{ox} *vs.* $-\log[\mathrm{H^+}]$ (Fig. 2) shows that the reaction rate decreases steadily with $-\log[\mathrm{H^+}]$, is saturated around $-\log[\mathrm{H^+}] \approx 6.79$–$7.75$ (pH $\approx$ 7.0–8.0) for $[\mathrm{Ni^{IV}L^3{}_2}]^{2+} \longrightarrow [\mathrm{Ni^{III}L^3{}_2}]^+$, while for $[\mathrm{Ni^{IV}L^2}]^{2+} \longrightarrow [\mathrm{Ni^{III}L^2}]^+$ a similar profile was observed with saturation around $-\log[\mathrm{H^+}] \approx 5.83$–$6.79$ (pH $\approx$ 6.0–7.0).

The deprotonated species, $[\mathrm{Ni^{IV}(L_x)}]^{2+}$ ($\mathrm{p}K_{\mathrm{h}} < 1.0$), would be expected to exist in the range pH 2.5–8.0. On the other hand, $\mathrm{p}K_2$ for the dissociation of $\mathrm{HS_2O_3}^-$, defined by equation (14), is

$$\mathrm{HS_2O_3}^- \rightleftharpoons \mathrm{H^+} + \mathrm{S_2O_3}^{2-} \qquad (14)$$

in the range 1.70–2.0.[17] The dependence of rate on $[\mathrm{H^+}]$ is thus expected to be solely governed by equilibrium (14). Since the reaction rate decreases with pH, it is reasonable to say that $\mathrm{S_2O_3}^{2-}$ has lower reactivity towards $[\mathrm{Ni^{IV}(L_x)}]^{2+}$ than does $\mathrm{HS_2O_3}^-$. Excluding protonation of the complex a plausible outer-sphere reaction mechanism is that in Scheme 2. The reduced species of the complexes would be protonated or deprotonated depending upon the pH of the medium and the extent of protonation (two or one) also depends upon the pH, governed by the pK values of the nickel(II) complexes (see below).* Scheme 2 leads to the rate law (19) where $[k_{\mathrm{ox}} = k_{\mathrm{obs}}/2n[\mathrm{S_2O_3}^{2-}]_{\mathrm{T}}]$.

$$[\mathrm{Ni^{IV}(L_x)}]^{2+} + \mathrm{HS_2O_3}^- \xrightarrow{k_3} [\mathrm{Ni^{III}(L_x)}]^+ + \mathrm{H^+} + \mathrm{S_2O_3}^- \qquad (15)$$

$$[\mathrm{Ni^{IV}(L_x)}]^{2+} + \mathrm{S_2O_3}^{2-} \xrightarrow{k_4} [\mathrm{Ni^{III}(L_x)}]^+ + \mathrm{S_2O_3}^- \qquad (16)$$

$$\mathrm{S_2O_3}^- + \mathrm{S_2O_3}^{2-} \overset{K_{\mathrm{rad}}}{\rightleftharpoons} \mathrm{S_4O_6}^{3-} \qquad (9)$$

At lower pH:

$$[\mathrm{Ni^{III}(L_x)}]^+ + \mathrm{S_4O_6}^{3-} \xrightarrow{\text{fast}} [\mathrm{Ni^{II}(L_x)}] + \mathrm{S_4O_6}^{2-} \qquad (17)$$

At higher pH:

$$[\mathrm{Ni^{IV}(L_x)}]^{2+} + \mathrm{S_4O_6}^{3-} \xrightarrow{\text{fast}} [\mathrm{Ni^{III}(L_x)}]^+ + \mathrm{S_4O_6}^{2-} \qquad (18)$$

Scheme 2

$$k_{\mathrm{ox}} = \frac{k_1[\mathrm{H^+}] + k_2K_2}{[\mathrm{H^+}] + K_2} \qquad (19)$$

Fitting of experimental data by equation (19) using a non-linear least-squares program was not satisfactory. Considering the $\mathrm{p}K_2$ of thiosulfurous acid ($\leqslant 2.0$), the rate saturation should occur at pH $\approx$ 3.0. Here the rate of reaction is highly sensitive to the pH of the medium over a wide range (pH 2.50–6.0). This implies the presence of another protic equilibrium. Since thiosulfurous acid is a dibasic acid, a third protic equilibrium is unthinkable for it. Again, the $\mathrm{p}K_{\mathrm{h}}$ of the nickel(IV) complexes is reported to be < 1.0. A reason for the pH dependence may be some outer-sphere complexation with buffer or some trace metal catalytic effect in the medium.[18] The possibility of a buffer effect was eliminated by varying the concentration of both phosphate and acetate buffers in the range (1.0–50.0) × 10^{-3} mol dm^{-3} with no significant change in rate. The catalytic effect of trace metals was also excluded by using $\mathrm{Na_2H_2edta}$ (1.0 × 10^{-4} mol dm^{-3}) as a masking agent without any change of rate. Thus we considered a protic equilibrium (20) involving the nickel(IV) complexes and the pH *vs.* rate profile then leads to the reaction sequence in Scheme 3 in the range pH 2.5–8.0.

$$[\mathrm{Ni^{IV}(HL_x)}]^{3+} \overset{K_{\mathrm{a}}}{\rightleftharpoons} [\mathrm{Ni^{IV}(L_x)}]^{2+} + \mathrm{H^+} \qquad (20)$$

$$[\mathrm{Ni^{IV}(HL_x)}]^{3+} + \mathrm{HS_2O_3}^- \xrightarrow{k_1} [\mathrm{Ni^{III}(HL_x)}]^{2+} + \mathrm{S_2O_3}^- + \mathrm{H^+} \qquad (21)$$

$$[\mathrm{Ni^{IV}(HL_x)}]^{3+} + \mathrm{S_2O_3}^{2-} \xrightarrow{k_2} [\mathrm{Ni^{III}(HL_x)}]^{2+} + \mathrm{S_2O_3}^- \qquad (22)$$

$$[\mathrm{Ni^{IV}(L_x)}]^{2+} + \mathrm{HS_2O_3}^- \xrightarrow{k_3} [\mathrm{Ni^{III}(L_x)}]^+ + \mathrm{H^+} + \mathrm{S_2O_3}^- \qquad (15)$$

$$[\mathrm{Ni^{IV}(L_x)}]^{2+} + \mathrm{S_2O_3}^{2-} \xrightarrow{k_4} [\mathrm{Ni^{III}(L_x)}]^+ + \mathrm{S_2O_3}^- \qquad (16)$$

Scheme 3

The rate law (23) is then derived. The best fit of the experimental data by the simplex optimisation program using equation (23) was achieved only by neglecting reaction (15) and the final form of the rate law is thus given by equation (24).

$$k_{\mathrm{ox}} = \frac{k_1[\mathrm{H^+}]^2 + (k_2K_2 + k_3K_{\mathrm{a}})[\mathrm{H^+}] + k_4K_2K_{\mathrm{a}}}{(K_{\mathrm{a}} + [\mathrm{H^+}])(K_2 + [\mathrm{H^+}])} \qquad (23)$$

$$k_{\mathrm{ox}} = \frac{k_1[\mathrm{H^+}]^2 + k_2K_2[\mathrm{H^+}] + k_4K_2K_{\mathrm{a}}}{(K_{\mathrm{a}} + [\mathrm{H^+}])(K_2 + [\mathrm{H^+}])} \qquad (24)$$

The parameters evaluated were: $k_1 = 25.2 \pm 0.8$, $k_2 = 8.26 \pm 0.30$ and $k_4 = (20.4 \pm 0.60) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}, $K_2 = (1.41 \pm 0.03) \times 10^{-2}$ mol dm^{-3} ($\mathrm{p}K_2 = 1.85$) and $k_{\mathrm{a}} = (1.22 \pm 0.04) \times 10^{-5}$ mol dm^{-3} ($\mathrm{p}K_{\mathrm{a}} = 4.91$) for $[\mathrm{Ni^{IV}L^3{}_2}]^{2+}$ reduction, and $k_1 = 18.5 \pm 0.50$, $k_2 = 5.27 \pm 0.20$ and $k_4 = (1.98 \pm 0.1) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}, $K_2 = (2.06 \pm 0.04) \times 10^{-2}$ mol dm^{-3} ($\mathrm{p}K_2 = 1.69$) and $K_{\mathrm{a}} = (5.30 \pm 0.09) \times 10^{-5}$ mol dm^{-3} ($\mathrm{p}K_{\mathrm{a}} = 4.28$) for $[\mathrm{Ni^{IV}L^2}]^{2+}$ reduction. The K_2 values for thiosulfurous acid $\mathrm{H_2S_2O_3}$ obtained for the oxidation of thiosulfate by two nickel(IV) complexes are in good agreement and also with reported values. The difference in $\mathrm{p}K_{\mathrm{a}}$ for $[\mathrm{Ni^{IV}L^3{}_2}]^{2+}$ and $[\mathrm{Ni^{IV}L^2}]^{2+}$ seems comparable to that for the corresponding nickel(III) complexes[3,4] (4.43 and 4.03 respectively) and the above findings will be discussed later.

Reduction of nickel(III)

The slower pH-dependent reaction at pH $\geqslant$ 6.0 for $[\mathrm{Ni^{IV}L^3{}_2}]^{2+}$ and pH $\geqslant$ 5.0 for $[\mathrm{Ni^{IV}L^2}]^{2+}$ was identified with the reduction of $[\mathrm{Ni^{III}(L_x)}]^+$ and confirmed by using electrochemically generated $[\mathrm{Ni^{III}L^2}]^+$ as reductant at pH > 6.0. Since thiosulfate shows no protic equilibrium in the region pH $\approx$ 4.0–8.0, the protonation must involve a protic equilibrium of the nickel(III) complex, see equation (2). As the dependence of rate on pH for this step is similar to that for the reduction of the nickel(IV) complexes (Fig. 3), the reaction events can be portrayed as in Scheme 4 and the rate equation (27) is derived. The solution of the latter was achieved by fitting the experimental data using a non-linear least-squares program. The parameters evaluated were: $k_5 = 11.94 \pm 0.30$ and $k_6 =$

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* The $\mathrm{p}K_1$ and $\mathrm{p}K_2$ values are 5.90 ± 0.05 and 7.80 ± 0.05 for $[\mathrm{Ni^{II}(H_2L^2)}]^{2+}$ and 7.80 ± 0.05 and 10.00 ± 0.05 for $[\mathrm{Ni^{II}(HL^3)_2}]^{2+}$.[2]

$$[\mathrm{Ni^{III}(HL}_x)]^{2+} + \mathrm{S_2O_3}^{2-} \xrightarrow{k_5} [\mathrm{Ni^{II}(HL}_x)]^{+} + \mathrm{S_2O_3} \qquad (25)$$

$$[\mathrm{Ni^{III}(L}_x)]^{+} + \mathrm{S_2O_3}^{2-} \xrightarrow{k_6} [\mathrm{Ni^{II}(L}_x)] + \mathrm{S_2O_3}^{-} \qquad (26)$$

Scheme 4

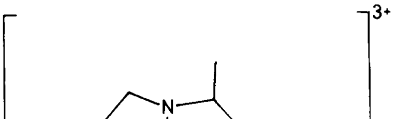
$$k_{\mathrm{ox}} = (k_5[\mathrm{H}^+] + k_6K'_{\mathrm{h}})/([\mathrm{H}^+] + K'_{\mathrm{h}}) \qquad (27)$$

(8.93 ± 0.20) × 10^{-2} dm^3 mol^{-1} s^{-1} and K'_{h} = (3.74 ± 0.08) × 10^{-5} mol dm^{-3} (pK'_{h} = 4.43) for $[\mathrm{Ni^{III}L^3}_2]^+$, and k_5 = 2.50 ± 0.03 and k_6 = (7.05 ± 0.3) × 10^{-3} dm^3 mol^{-1} s^{-1} and K'_{h} = (1.01 ± 0.01) × 10^{-4} mol dm^{-3} (pK'_{h} = 4.00) for $[\mathrm{Ni^{III}L^2}]^+$. Here also there is good agreement between the kinetically evaluated and reported pK'_{h} values which strongly supports the proposed mechanism.

The present study is interesting from the viewpoint of the unusual type of protonation of the nickel(IV) complexes {pK_{a} = 4.91 for $[\mathrm{Ni^{IV}L^3}_2 \cdots \mathrm{H}]^{3+}$ and 4.28 for $[\mathrm{Ni^{IV}L^2} \cdots \mathrm{H}]^{3+}$}. At pH > 3.0 the protic equilibrium associated with the thiosulfate reductant is absent and protonation of the oxime group in the nickel(IV) complexes is expected to occur at lower pH than those observed for the corresponding nickel(III) analogue. Protonation of these nickel(IV) complexes at pH > 1.0 appears somewhat puzzling and requires proper justification. Spectral and cyclic voltammetric studies[2] reveal that the protonations having pK_{a} 4.28 and 4.91 do not involve the oxime protons. It is suggested that $[\mathrm{Ni^{IV}(L}_x)]^{2+}$ participates *via* an acid–base interaction through 'outside' protonation. The situation is comparable to metal–nitrogen (peptide) bond formation where, if the metal ion is inert to substitution, 'outside' protonation can occur through a kinetic intermediate.[19–21] In fact the redox reactivity of copper(III)-peptide complexes is enhanced owing to this phenomenon. The protonation of $[\mathrm{Ni^{IV}(L}_x)]^{2+}$ is considered to involve a hydrogen-bonded intermediate between the oximato oxygen atom (=N–O) and a vicinal imino nitrogen atom in the pseudo-octahedral arrangement **IV** in which the Ni$^{\mathrm{IV}}$–N bond is not substantially weakened.

In an attempt to determine the protic equilibrium associated with this 'outside' protonation, potentiometric pH titrations were carried out with both the $[\mathrm{Ni^{IV}(L}_x)]^{2+}$ complexes in the presence of a fixed concentration of strong acid. The titration curves (Fig. 4) showed that the complexes behave as weak bases in the range pH 2.5–8.0. At pH > 8.0 the titration curves deviate from the expected sharp change in pH (near the end-point) with added alkali and this may arise from non-equilibrium redox decomposition of the complexes. The pK values were evaluated by plotting pH *vs.* log [(1 − $\bar{n}_{\mathrm{H}}$)/$\bar{n}_{\mathrm{H}}$], where $\bar{n}_{\mathrm{H}}$ = average number of hydrogen atoms bound to $[\mathrm{Ni^{IV}(L}_x)]^{2+}$ according to the Bjerrum ($\bar{n}_{\mathrm{H}}$)$_{\frac{1}{2}}$ method.[22] The evaluated pK values were 6.0 ± 0.6 and 5.2 ± 0.5 for $[\mathrm{Ni^{IV}L^3}_2 \cdots \mathrm{H}]^{3+}$ and $[\mathrm{Ni^{IV}L^2} \cdots \mathrm{H}]^{3+}$ respectively. These are slightly higher than the corresponding values obtained kinetically which may be due to the two different methods of evaluation and the solution composition.

There are hardly any reports on the lability of nickel-(IV) and -(III) complexes of $\mathrm{H_2L^2}$ and $\mathrm{HL^3}$, although the axial positions of nickel(III) complexes are expected to be relatively labile (< 10^2 s^{-1}). In accordance with this, the preferred mechanism for the nickel-(IV)/and -(III) complexes would be outer sphere. Earlier studies on such complexes support this although in a few cases inner-sphere electron transfer has been suggested.[3,12,23] Unfortunately no direct spectral evidence has been gathered to support any inner-sphere route and this is also true of the present investigation. Comparison of the reactivities of $[\mathrm{Ni^{IV}(L}_x) \cdots \mathrm{H}]^{3+}$, a hydrogen-bonded species, towards $\mathrm{HS_2O_3}^-$ and $\mathrm{S_2O_3}^{2-}$ (Table 2) showed that $\mathrm{HS_2O_3}^-$ is much more reactive than $\mathrm{S_2O_3}^{2-}$. In the pH range where $\mathrm{HS_2O_3}^-$ is expected to exist (pH < 3.50) the reduced species of the complex is $[\mathrm{Ni^{II}(H_2L}_x)]^{2+}$ requiring one more proton for its formation.



IV

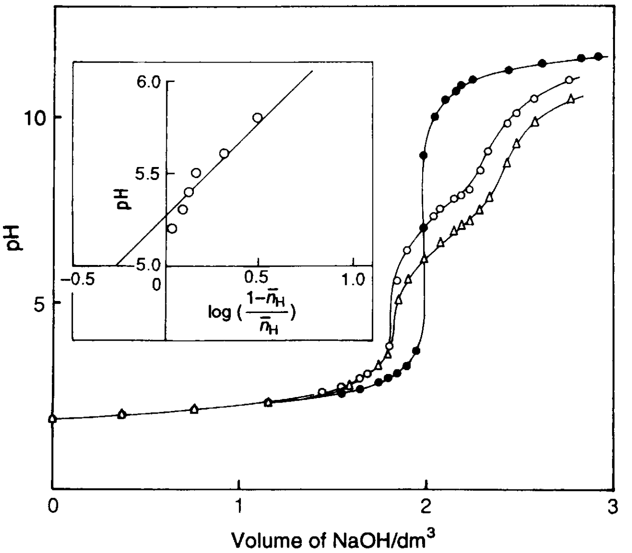


Fig. 4 Plots of pH *vs.* volume of alkali (dm^3) at I = 0.1 mol dm^{-3} ($\mathrm{NaClO_4}$), 22.8 ± 0.2 °C using [NaOH] = 0.1015 mol dm^{-3} and total initial solution volume 25.0 dm^3 for [$\mathrm{HClO_4}$] = 8.04 × 10^{-3} mol dm^{-3} (●), $[\mathrm{Ni^{IV}L^3}_2{}^{2+}]$ = 1.04 × 10^{-3} mol dm^{-3} and [$\mathrm{HClO_4}$] = 8.04 × 10^{-3} mol dm^{-3} (○) and $[\mathrm{Ni^{IV}(L^2)^{2+}}]$ = 1.0 × 10^{-3} mol dm^{-3} and [$\mathrm{HClO_4}$] = 8.04 × 10^{-3} mol dm^{-3} (△). The inset shows a plot of pH *vs.* log [(1 − $\bar{n}_{\mathrm{H}}$)/$\bar{n}_{\mathrm{H}}$] for $[\mathrm{Ni^{IV}L^2}]^{2+}$

Table 2 Reactivity of different thiosulfate species

	k_{12}/dm^3 mol^{-1} s^{-1}	
Oxidant	$\mathrm{HS_2O_3}^-$	$\mathrm{S_2O_3}^{2-}$
$[\mathrm{Ni^{IV}L^3}_2 \cdots \mathrm{H}]^{3+}$	25.2 ± 0.80	8.26 ± 0.30
$[\mathrm{Ni^{IV}L^3}_2]^{2+}$	—	(20.4 ± 0.60) × 10^{-2}
$[\mathrm{Ni^{III}L^3}_2]^{+}$	—	(8.93 ± 0.2) × 10^{-2}
$[\mathrm{Ni^{III}L^3(HL^3)}]^{2+}$	—	11.94 ± 0.30
$[\mathrm{Ni^{IV}L^2} \cdots \mathrm{H}]^{3+}$	18.54 ± 0.50	5.27 ± 0.20
$[\mathrm{Ni^{IV}L^2}]^{2+}$	—	(1.98 ± 0.1) × 10^{-2}
$[\mathrm{Ni^{III}L^2}]^{+}$	—	(7.05 ± 0.3) × 10^{-3}
$[\mathrm{Ni^{III}(HL^2)}]^{2+}$	—	2.50 ± 0.03

If one assumes that $\mathrm{HS_2O_3}^-$ reacts with $[\mathrm{Ni^{IV}(L}_x) \cdots \mathrm{H}]^{3+}$ through the formation of a hydrogen-bonded adduct in a pre-equilibrium step involving the hydrogen atom on $\mathrm{HS_2O_3}^-$ and oximato oxygen atom (=N–O$^-$) of the ligand, there will be ready availability of a proton. The formation of a hydrogen-bonded intermediate between the complex and $\mathrm{HS_2O_3}^-$ would provide a low-energy electron-transfer path resulting in faster reaction of $[\mathrm{Ni^{IV}(L}_x) \cdots \mathrm{H}]^{3+}$ towards $\mathrm{HS_2O_3}^-$ than $\mathrm{S_2O_3}^{2-}$. This explanation has been highlighted for many reactions of

Table 3 Cross-reaction kinetic data for the oxidation of $S_2O_3^{2-}$ by different oxidants

	Oxidant	E_f/V	r/Å	k_{11}/dm^3 mol^{-1} s^{-1}	k/dm^3 mol^{-1} s^{-1} exptl.	k/dm^3 mol^{-1} s^{-1} calc.	k_{-d}/dm^3 mol^{-1} s^{-1}
1	$[Os^{III}(4,7\text{-dmphen})_3]^{3+}$	0.653[a]	7.4	2.0×10^9	0.997	2.09	8.58×10^{10}
2	$[Os^{III}(5,6\text{-dmphen})_3]^{3+}$	0.776[a]	7.4	2.0×10^9	31.7	150.64	2.56×10^{10}
3	$[Os^{III}(phen)_3]^{3+}$	0.840[a]	6.7	2.0×10^9	1.90×10^2	1.62×10^3	1.13×10^{10}
4	$[Os^{III}(cphen)_3]^{3+}$	0.944[a]	7.4	2.0×10^9	1.22×10^4	3.51×10^4	1.28×10^{10}
5	$[Fe^{III}(bipy)_3]^{3+}$	1.05[a]	6.8	5.0×10^8	2.05×10^5	4.54×10^5	3.44×10^9
6	$[Ni^{III}(tacn)_2]^{3+}$	0.952[a]	3.8	6.0×10^3	1.40×10^3	1.10×10^3	1.15×10^9
7	$[Ni^{III}L^1]^{2+}$	0.490[b]	5.1	6.0×10^2	10.4×10^{-2}	1.78×10^{-4}	3.03×10^{12}
8	$[Ni^{IV}L^2]^{2+}$	0.654[c]	5.1	1.0×10^5	1.98×10^{-2}	7.53×10^{-2}	2.49×10^9
9	$[Ni^{IV}L^3{}_2]^{2+}$	0.630[d]	5.1	8.0×10^4	20.4×10^{-2}	3.35×10^{-2}	6.63×10^{10}
10	$[Ni^{III}L^2]^+$	0.420[c]	5.1	2.0×10^3	7.05×10^{-3}	7.23×10^{-6}	9.30×10^{12}
11	$[Ni^{III}(HL^2)]^{2+}$	0.640[c]	5.1	1.0×10^3	2.50	8.74×10^{-3}	5.47×10^{11}
12	$[Ni^{III}L^3{}_2]^+$	0.30[d]	5.1	8.0×10^3	8.93×10^{-2}	1.58×10^{-7}	1.36×10^{16}
13	$[Ni^{III}L^3(HL^3)]^{2+}$	0.63[d]	5.1	5.0×10^2	11.94	4.98×10^{-3}	3.88×10^{12}
14	$[Mn^{III}(cdta)]^-$	0.814[b]	5.02	0.70	0.18	1.21×10^{-2}	2.16×10^{-7}

$E°$ ($S_2O_3^-$–$S_2O_3^{2-}$) = 1.30 V, k_{11} (S_2O_3–$S_2O_3^{2-}$) = 2.3×10^{5} dm^3 mol^{-1} s^{-1},[25] $k_{-d} = k_{exptl}/K_{12}$ for the oxidation of $S_2O_3^{2-}$ by different oxidants. For reactions 1–6, 25 °C, I = 0.10 mol dm^{-3}; for 7 and 14, 30 °C, I = 0.2 mol dm^{-3}; and for 8–13, 20 °C and I = 0.2 mol dm^{-3}, $Z = 10^{11}$ dm^3 mol^{-1} s^{-1}. Abbreviations: 4,7-, 5,6-dmphen = 4,7-,5,6-dimethyl-1,10-phenanthroline; cphen = 5-chloro-1,10-phenanthroline; bipy = 2,2′-bipyridine; tacn = 1,4,7-triazacyclononane; cdta = *trans*-cyclohexane-1,2-diyldinitrilotetraacetate. [a] Ref. 25. [b] Ref. 12. [c] Ref. 4. [d] Ref. 3.

these nickel(IV) complexes.[3,23] The higher reactivity of $HS_2O_3^-$ than $S_2O_3^{2-}$ towards $[Ni^{IV}(L_x)]^{2+}$ could be explained in similar fashion. Again the reactivity of $[Ni^{IV}(L_x)]^{2+}$ toward $S_2O_3^{2-}$ would be expected to be slightly higher than that toward $[Ni^{III}(HL_x)]^{2+}$ on the basis of thermodynamic potential (comparable to each other) and electron exchange-rate $\{[Ni^{IV}(L_x)]^{2+} > [Ni^{III}(HL_x)]^{2+}\}$ considerations. Experimentally, however, it has been found that $[Ni^{III}(HL_x)]^{2+}$ is much more reactive towards electron transfer than is $[Ni^{IV}(L_x)]^{2+}$. This can be explained by considering the higher lability of the nickel(III) complexes than those of nickel(IV) and also the ready availability of the hydrogen atom on $[Ni^{III}(HL_x)]^{2+}$ since the reduction to nickel(II) in the low pH region (pH ≈ 3–5) requires additional protonation. Similarly the higher reactivity of $[Ni^{III}(HL_x)]^{2+}$ than that of $[Ni^{III}(L_x)]^+$ can be justified although some electrostatic considerations may come into play.

The pattern of the reactions (outer- or inner-sphere) of the nickel-(IV) and -(III) complexes of HL^3 and H_2L^2 could be rationalised by correlating the kinetic data to the Marcus cross-relations [equations (28)–(32)].[24] These correlations could be

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{\frac{1}{2}}W_{12} \tag{28}$$

$$E° = 0.0582 \log K_{12} \text{ at } 20\ °\text{C} \tag{29}$$

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4[\ln(k_{11}k_{22}/Z^2) + (w_{11} + w_{22})/RT]} \tag{30}$$

$$w_{ij} = \frac{4.23\, Z_iZ_j}{a(1 + 0.328\, a\, I^{\frac{1}{2}})} \tag{31}$$

$$W_{12} = \exp[(-w_{12} - w_{21} + w_{11} + w_{22})/2RT] \tag{32}$$

made only for the reactions of $[Ni^{IV}(L_x)]^{2+}$, $[Ni^{III}(HL_x)]^{2+}$ and $[Ni^{III}(L_x)]^+$ towards $S_2O_3^{2-}$ as they involve well determined potentials and self-exchange rate constants. In these equations k_{11} is the self-exchange rate constant for the couple $S_2O_3^{2-}$–$S_2O_3^-$, k_{22} is the self-exchange rate constant for the various oxidising complexes and K_{12} is the equilibrium constant for the electron-transfer reaction, calculated by equation (29) at 20 °C; Z in equation (30) is the collision frequency, Z_i and Z_j are the ionic charges of the respective species, R is the universal gas constant and a is the centre-to-centre distance (Å) when the reaction species are in contact. The radius of the nickel-(IV) and -(III) complexes with the ligands HL^3 and H_2L^2 is taken as 5.1 Å,[23] that of $S_2O_3^{2-}/S_2O_3^-$ is reported to be 3.0 Å and k_{11} = 2.3×10^5 dm^3 mol^{-1} s^{-1}.[25] With the help of these parameters, reported $E°$ values and electron self-exchange rate constants, the cross electron-transfer rate constants (k_{12}) for several positively charged complexes including our reactions were calculated and are summarised in Table 3. A close inspection of Table 3 reveals that there is an excellent agreement between the experimental and calculated values of k_{12} for the oxidation of $S_2O_3^{2-}$ by $[Ni^{IV}L^3{}_2]^{2+}$ and $[Ni^{IV}L^2]^{2+}$. For other reactions involving $[Ni^{III}(HL_x)]^{2+}$ and $[Ni^{III}(L_x)]^+$–$S_2O_3^{2-}$ the experimental values are higher by 2–5 orders of magnitude than the calculated ones. Thus on the basis of these calculations it is suggested that $[Ni^{IV}(L_x)]^{2+}$ and other oxidants react by an outer-sphere mechanism, whereas $[Ni^{III}(L_x)]^+$ and $[Ni^{III}(HL_x)]^{2+}$ react by a different mechanism.

The inner-sphere mechanism may be explained by considering either a weak overlap between the filled p orbital on oxygen and a vacant d orbital on sulfur, or partial unwrapping of one of the co-ordinated nitrogen atoms. The latter explanation arises from the lower electron-transfer rate compared to the lability of the nickel(III) complexes (10^2 s^{-1}). As there is no direct evidence, it is difficult to choose one over the other.

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