Kinetics and Mechanisms of Reduction of a Sexidentate Di(oxime–imine) Complex of Nickel(IV) with Two-electron Reductants, 1,2-Dihydroxybenzene and 1,4-Dihydroxybenzene †

Sheila F. Munn, A. Martin Lannon, Mauro C. M. Laranjeira, and A. Graham Lappin *
Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556, U.S.A.

The kinetics and mechanisms of reduction of a nickel(IV) di(oxime–imine) complex, $[Ni^{IV}L]^{2+}$ (H_2L = 3,14-dimethyl-4,7,10,13-tetra-azahexadeca-3,13-diene-2,15-dione dioxime), by 1,2-dihydroxybenzene (H_2Z) and 1,4-dihydroxybenzene (H_2Q) are reported. Both reactions proceed by consecutive one-electron transfers and kinetic traces are biphasic with quantitative formation of nickel(III) intermediates, $[Ni^{III}L]^+$ and $[Ni^{III}(HL)]^{2+}$ depending on the pH. The dominant pathways for reduction of both nickel(IV) and nickel(III) involve the reductant anions HZ^- and HQ^-. Reactions of nickel(IV) are outer-sphere in nature while those of nickel(III) proceed by an inner-sphere pathway. Preliminary results on the oxidation of the corresponding nickel(II) complex by thallium(III) indicate that no detectable intermediate oxidation-state species is formed in this reaction.

The nickel(IV) di(oxime–imine) complex, $[Ni^{IV}L]^{2+}$, with the sexidentate ligand 3,4-dimethyl-4,7,10,13-tetra-azahexadeca-3,13-diene-2,15-dione dioxime, H_2L, forms with oxime deprotonation and is substitution inert even in strongly acidic media.[1] It can be optically resolved consistent with a low-spin d^6 electronic configuration.[2] Cyclic voltammetry results [3,4] indicate that the complex undergoes reversible two-electron reduction at pH < 5 [equation (1)] with a potential of 0.94 V

$$[Ni^{IV}L]^{2+} + 2e^- + 2H^+ \rightleftharpoons [Ni^{II}(H_2L)]^{2+} \qquad (1)$$

(*vs.* n.h.e., normal hydrogen electrode, at 25 °C and 0.10 mol dm^{-3} ionic strength) but kinetic studies with the two-electron reductant ascorbic acid,[5] and with one-electron reductants,[4,6–8] show dominant pathways involving consecutive one-electron transfers with formation of nickel(III) intermediates. The nickel(IV) one-electron reduction potential [equation (2)] is

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

0.65 V. Protonation of the complex $[Ni^{III}L]^+$ occurs with a pK_h of 4.05 and reduction potentials for $[Ni^{III}L]^+$ and $[Ni^{III}(HL)]^{2+}$ are 0.42 and 0.64 V respectively.[4] These are reflected in the relative reactivities of the nickel(III) complexes.

In this paper, the kinetics and mechanisms of reduction of $[Ni^{IV}L]^{2+}$ by the two-electron reductants 1,4-dihydroxybenzene (H_2Q) and 1,2-dihydroxybenzene (H_2Z) are presented. The reductants H_2Q and H_2Z have two-electron potentials [equation (3)] of 0.699 and 0.791 V [9] respectively where Q′ and

$$Q' \text{ or } Z' + 2e^- + 2H^+ \rightleftharpoons H_2Q \text{ or } H_2Z \qquad (3)$$

Z′ are the dehydro-derivatives, *p*- and *o*-benzoquinone. It is of considerable interest to discover whether these two-electron reductants will react like ascorbic acid by two single-electron transfer reactions or whether a single two-electron transfer is possible. Some preliminary data on the oxidation of the nickel(II) complex $[Ni(H_2L)]^{2+}$ by thallium(III) are also presented.

Experimental

The nickel(IV) complexes with H_2L were obtained as perchlorate salts by methods outlined previously.[1,5] Solutions of $[Ni^{IV}L]^{2+}$ were standardised spectrophotometrically using literature absorption coefficients: λ/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) 500 (6 300), 430 (5 960). 1,2-Dihydroxybenzene was crystallised (×3) from ethanol; 1,4-dihydroxybenzene (B.D.H.) was of AnalaR grade as were the acetate buffers, $NaClO_4$, and $HClO_4$ used in solution preparations. All solutions were prepared immediately prior to use and were bubbled with chromium(II)-scrubbed N_2 gas or argon for at least 15 min to suppress aerial oxidation of the reductants.

The reaction stoicheiometries were determined by the addition, at pH 4.0, of aliquots of reductant H_2Z or H_2Q to a standard $[Ni^{IV}L]^{2+}$ solution which was then restandardised.

Kinetic measurements were made in 1.0×10^{-2} mol dm^{-3} acetate buffer at an ionic strength of 0.10 mol dm^{-3} ($NaClO_4$) unless otherwise stated. Experiments were run under pseudo-first-order conditions with an excess of reductant $\{[Ni^{IV}L^{2+}] \simeq 5.0 \times 10^{-5}$ mol dm^{-3}; $[H_2Z]_T = 5 \times 10^{-4}$—$50 \times 10^{-4}$ mol dm^{-3}, $[H_2Q]_T = 2 \times 10^{-4}$—$500 \times 10^{-4}$ mol $dm^{-3}\}$ and were monitored at the absorption maximum of the nickel(IV) complex at 500 nm, or at the $[Ni^{IV}L]^{2+}/[Ni^{III}L]^+$ isosbestic around 390 nm using an Applied Photophysics stopped-flow spectrophotometer thermostatted at 25.0 ± 0.1 °C. The absorbance changes, recorded on a Tektronix 5111 storage oscilloscope showed biphasic behaviour. Rate constants for the slower phase were, in some cases, evaluated directly from the latter 25% of the reaction trace at 500 or 390 nm by first-order treatment. Results from both wavelengths showed excellent agreement. Rate constants for the faster phase were obtained by a curve-fitting procedure, analyzing the absorbance data at 500 nm on the basis of consecutive first-order reactions.[10]

In the kinetic experiments, the pH was varied from 3.5 to 6.5 and was measured, after reaction, using an E.I.L. 7055 pH meter. A saturated calomel (NaCl) reference electrode (s.c.e.) was used and hydrogen-ion concentrations were evaluated using the relationship $\log [H^+] = 0.02 - pH$, correcting for both hydrogen-ion activity and the liquid-junction potential.

Results and Discussion

Reaction Stoicheiometry and Intermediates.—The stoicheiometric behaviour of the reduction of $[Ni^{IV}L]^{2+}$ by H_2Z or H_2Q in mildly acidic media indicates that 0.95 ± 0.03 and 0.96 ± 0.02 mol, respectively, of nickel(IV) are consumed for each mol of reductant. This is consistent with the formation of nickel(II) and the dehydro-derivatives Z′ and Q′ [equations (4)

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† *Non-S.I. unit employed*: cal = 4.184 J.

Table 1. Spectrophotometric parameters for Ni^{IV}, Ni^{III}, and Ni^{II}

Complex	λ/nm	ε/dm³ mol⁻¹ cm⁻¹
$[Ni^{IV}L]^{2+}$	500	6 300 [a]
	430	5 960 [a]
	390	3 000 [b]
$[Ni^{III}(HL)]^{2+}$	490	2 980 [b]
$[Ni^{III}L]^{+}$	505	2 890 [b]
	398	3 000 [b]
$[Ni^{II}(H_2L)]^{2+}$	780	36 [a]
	500	78 [a]

[a] Ref. 1. [b] Ref. 4.

and (5)] and is the expected result based on thermodynamic considerations.

$$[Ni^{IV}L]^{2+} + H_2Z \longrightarrow [Ni^{II}(H_2L)]^{2+} + Z' \quad (4)$$

$$[Ni^{IV}L]^{2+} + H_2Q \longrightarrow [Ni^{II}(H_2L)]^{2+} + Q' \quad (5)$$

Reactions with both reductants show very similar biphasic behaviour at 500 nm. Each phase accounts for approximately 50% of the total absorbance change at that wavelength. Above pH 4.5, the more rapid phase has an isosbestic at 390 nm which moves to 410 nm on decreasing the pH. This behaviour is characteristic of the formation, in the course of the reaction, of a nickel(III) intermediate, $[Ni^{III}L]^+$, which undergoes protonation [equation (6)] with a pK_h of 4.05.[4] In the catechol

$$[Ni^{III}(HL)]^{2+} \overset{K_h}{\rightleftharpoons} [Ni^{III}L]^+ + H^+ \quad (6)$$

reduction at pH 4.7, a point-by-point spectrum of the apparent break point between the fast and slow phases reveals characteristics of the nickel(III) species, but, since the reactions are not well separated, the continuing presence of some nickel(IV) is also indicated. Quantitative formation of the nickel(III) intermediate implies that the reduction of $[Ni^{IV}L]^{2+}$ by H_2Z and H_2Q takes place in two consecutive one-electron steps and in this respect is similar to the reduction by ascorbic acid, H_2A.[5]

Reaction Kinetics.—With the reductants H_2Q and H_2Z the absorbance changes are complex and increase in rate with pH. The faster phase which has the isosbestic around 390 nm and can be identified as nickel(IV) reduction, increases in rate with pH more quickly than the slower phase, nickel(III) reduction, and allows some separation of the two processes at higher pH.

Under the pseudo-first-order conditions of the study, both processes, reduction of nickel(IV) and reduction of nickel(III), were treated as first-order reactions and thus a scheme [equation (7)] is derived. Good estimates for k_{III} were obtained by first-order plots from the last 25% of the reaction studied at 500 or 390 nm and good agreement was found for data from both wavelengths. The absorbance change at 500 nm also affords information on k_{IV} and, at any point in time, is given by the sum of the absorbances of nickel(IV) and nickel(III) since nickel(II) complexes have a relatively small absorbance in this region. Spectrophotometric parameters for the complexes are presented in Table 1.

$$Ni^{IV} \xrightarrow{k_{IV}} Ni^{III} \xrightarrow{k_{III}} Ni^{II} \quad (7)$$

The absorbance, A, at 500 nm is thus given by equation (8)

$$Al^{-1} = \varepsilon_{Ni^{IV}}[Ni^{IV}] + \varepsilon_{Ni^{III}}[Ni^{III}] \quad (8)$$

Table 2. Pseudo-first-order rate constants for reduction of nickel(IV) and nickel(III) by 1,2- and 1,4-dihydroxybenzene

pH	$10^3[H_2Z]_T$/mol dm⁻³	$2k_{IV}$/s⁻¹	$2k_{III}$/s⁻¹
1.19	3.66	—	0.143 ± 0.021 [a]
1.43	3.66	—	0.138 ± 0.018 [a]
3.62	4.93	0.62 ± 0.09	0.55 ± 0.05
4.03	4.93	1.73 ± 0.16	0.72 ± 0.03
4.25	4.93	2.71 ± 0.31	0.79 ± 0.05
4.45	4.93	4.19 ± 0.36	0.84 ± 0.03
4.62	4.93	6.46 ± 0.72	0.98 ± 0.06
4.62	4.80	6.77 ± 0.78	0.62 ± 0.04
4.63	2.88	3.76 ± 0.80	0.37 ± 0.06
4.64	1.92	2.32 ± 0.74	0.26 ± 0.07
4.64	0.48	0.65 ± 0.12	0.070 ± 0.009
4.64	0.96	1.26 ± 0.14	0.125 ± 0.008
4.74	4.93	6.90 ± 0.49	0.96 ± 0.02
5.02	4.93	(8.9 ± 1.17) [b]	1.10 ± 0.09
5.20	4.93	(12.3 ± 1.46) [b]	1.31 ± 0.09
5.54	4.93	—	1.22 ± 0.14
5.66	4.93	—	1.87 ± 0.19
5.92	4.93	—	2.27 ± 0.31
pH	$10^3[H_2Q]_T$/mol dm⁻³	$2k_{IV}$/s⁻¹	$2k_{III}$/s⁻¹
1.20	3.23	—	0.53 ± 0.03 [a]
1.36	3.23	—	0.73 ± 0.05 [a]
3.44	4.87	1.19 ± 0.22	0.99 ± 0.13
4.02	4.87	1.89 ± 0.17	1.80 ± 0.07
4.24	4.87	3.17 ± 0.30	2.03 ± 0.09
4.43	4.87	4.63 ± 0.28	1.97 ± 0.02
4.62	4.87	5.36 ± 0.50	2.10 ± 0.09
4.76	4.87	8.52 ± 0.62	2.21 ± 0.05
4.96	4.87	10.71 ± 0.72	2.35 ± 0.04
5.05	50.0	(97 ± 5.3) [b]	23.6 ± 0.1
5.06	25.1	(52 ± 3.4) [b]	12.3 ± 0.2
5.06	10.1	22.1 ± 1.2	4.65 ± 0.03
5.06	2.01	4.3 ± 0.35	0.97 ± 0.03
5.06	0.20	0.5 ± 0.03	0.095 ± 0.001
5.19	4.87	19.5 ± 1.16	2.09 ± 0.02
5.42	3.97	18.3 ± 1.15	2.33 ± 0.03
6.20	4.87	(73 ± 5.0) [b]	7.63 ± 0.14

[a] Measured only at $Ni^{IV/III}$ isosbestic. [b] Values in parentheses are uncertain.

which can be rewritten in terms of the consecutive first-order treatment as equation (9), where $[Ni^{IV}L^{2+}]_0$ is the initial

$$Al^{-1} = [Ni^{IV}L^{2+}]_0[\varepsilon_{Ni^{IV}}(k_{III} - k_{IV})e^{-k_{IV}t} - \varepsilon_{Ni^{III}}k_{IV}(e^{-k_{IV}t} - e^{-k_{III}t})]/(k_{III} - k_{IV}) \quad (9)$$

nickel(IV) concentration and l is the path-length of the stopped-flow spectrophotometer, 2.03 ± 0.01 cm. The absorbance data for the reaction traces were fitted to equation (9) using an iterative procedure for k_{IV} and the value for k_{III} obtained from the final 25% of the reaction, until calculated and observed absorbances were within 5% and the deviations showed no trend with time. Rate constants evaluated by this method are presented in Table 2.

Nickel(IV) *Reactions.*—The faster of the two processes under most of the observed conditions shows a first-order dependence on reductant concentration and is identified with the reduction of nickel(IV), $[Ni^{IV}L]^{2+}$, to nickel(III). In the reactions, a strong pH dependence is noted in the Figure. This

$$H_2Q \text{ or } H_2Z \overset{K_a}{\rightleftharpoons} HQ^- \text{ or } HZ^- + H^+ \quad (10)$$

Table 3. Rates of reduction (rate constants in dm^3 mol^{-1} s^{-1}) of nickel(IV) and nickel(III) complexes by two-electron reductants at 25.0 °C and 0.10 mol dm^{-3} ($NaClO_4$)

Reductant	Oxidant		
	$[Ni^{IV}L]^{2+}$	$[Ni^{III}(HL)]^{2+}$	$[Ni^{III}L]^{+}$
H_2Z	30 (60) [a,b]	17 [c]	—
H_2Q	220 (270) [a,b]	1.0×10^2 [c]	—
HZ^- obs.	2.5×10^7 (4.8×10^7) [a,d]	1.5×10^7 (1.5×10^7) [a,e]	2.9×10^5 (1.1×10^5) [a,f]
calc.	5.1×10^7 [d]	3.9×10^6 [e]	9.8×10^4 [f]
HQ^- obs.	6.6×10^7 (6.4×10^7) [a,d]	1.3×10^8 (1.7×10^8) [a,e]	2.7×10^6 (4.1×10^5) [a,f]
calc.	7.0×10^7 [d]	8.9×10^6 [e]	3.4×10^4 [f]
HA^-	—	1.5×10^5 [e,g]	6.6×10^3 [f,g]

[a] Ref. 24. [b] k_{IVa}. [c] k_{IIIa}. [d] k_{IVb}. [e] k_{IIIb}. [f] k_{IIIc}. [g] Ref. 5.

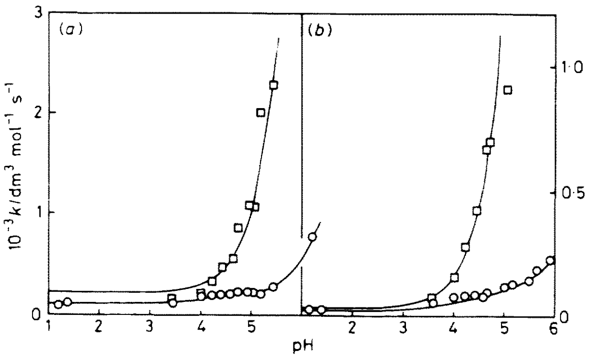

Figure. Plots of second-order rate constants against pH for reduction of nickel(IV) (□) and nickel(III) (○) by 1,4-dihydroxybenzene (*a*) and 1,2-dihydroxybenzene (*b*)

corresponds to a dominant $[H^+]^{-1}$ term and suggests that the principal reductants are the HZ^- and HQ^- ions with minor pathways for H_2Z and H_2Q, equations (11) and (12). The derived rate expression (13) allows evaluation of the rate

$$[Ni^{IV}L]^{2+} + H_2Q \text{ or } H_2Z \xrightarrow{k_{IVa}} [Ni^{III}L]^+ + HQ^{\cdot} \text{ or } HZ^{\cdot} + H^+ \quad (11)$$

$$[Ni^{IV}L]^{2+} + HQ^- \text{ or } HZ^- \xrightarrow{k_{IVb}} [Ni^{III}L]^+ + HQ^{\cdot} \text{ or } HZ^{\cdot} \quad (12)$$

$$\frac{-d[Ni^{IV}]}{dt} = 2\frac{k_{IVa}[H^+] + k_{IVb}K_a}{[H^+] + K_a}[H_2Q \text{ or } H_2Z][Ni^{IV}] \quad (13)$$

constants k_{IVa} and k_{IVb} as shown in Table 3 using pK_a values of 9.23 for H_2Z [11] and 9.85 for H_2Q.[12]

The dominant pathways involve reductants HZ^- and HQ^- rather than the protonated forms in agreement with the ease of oxidation of the species from thermodynamic considerations. Indeed for H_2Z, the reaction rate is too close to the nickel(III) rate to allow accurate detection. In common with other studies of these two reductants,[13,14] it is easier to oxidize derivatives of 1,4-dihydroxybenzene than 1,2-dihydroxybenzene.

Nickel(III) *Reactions*.—The slower of the two processes, reduction of nickel(III), is also first order in the reductant concentrations and the pH dependence is complex with an overall increase in reaction rate with increasing pH, but this is much less dramatic than in the nickel(IV) reactions, Figure. There appears to be a plateau around pH 4 and this may be explained by the superposition of the pK_h of nickel(III), equation (6), with $[Ni^{III}(HL)]^{2+}$ more reactive than $[Ni^{III}L]^+$, on a dominant reductant anion pathway, equations (14)—(16). The derived rate expression (17) allows evaluation of

$$[Ni^{III}(HL)]^{2+} + H_2Q \text{ or } H_2Z \xrightarrow{k_{IIIa}} [Ni^{II}(HL)]^+ + HQ^{\cdot} \text{ or } HZ^{\cdot} + H^+ \quad (14)$$

$$[Ni^{III}(HL)]^{2+} + HQ^- \text{ or } HZ^- \xrightarrow{k_{IIIb}} [Ni^{II}(HL)]^+ + HQ^{\cdot} \text{ or } HZ^{\cdot} \quad (15)$$

$$[Ni^{III}L]^+ + HQ^- \text{ or } HZ^- \xrightarrow{k_{IIIc}} [Ni^{II}L] + HQ^{\cdot} \text{ or } HZ^{\cdot} \quad (16)$$

$$\frac{-d[Ni^{III}]}{dt} = 2\left[\frac{k_{IIIa}[H^+]^2 + k_{IIIb}K_a[H^+] + k_{IIIc}K_aK_h}{([H^+] + K_a)([H^+] + K_h)}\right][H_2Q \text{ or } H_2Z][Ni^{III}] \quad (17)$$

the rate constants k_{IIIa}, k_{IIIb}, and k_{IIIc} as shown in Table 3, using a pK_h of 4.05 for nickel(III).

As with nickel(IV), reactions of the protonated reductants are slow and pathway (18) involving reaction with the least reactive nickel(III) species can be ignored. Again, derivatives

$$[Ni^{III}L]^+ + H_2Q \text{ or } H_2Z \longrightarrow [Ni^{II}L] + HQ^{\cdot} \text{ or } HZ^{\cdot} + H^+ \quad (18)$$

of 1,4-dihydroxybenzene react faster than those of 1,2-dihydroxybenzene.

The Organic Radicals.—The fates of the organic radicals $HQ^{\cdot}$ and $HZ^{\cdot}$ (*p*- and *o*-$HOC_6H_4O^{\cdot}$) are of some interest and importance. In the one-electron reduction of $[Ni^{IV}L]^{2+}$ the immediate products are solvent caged $[Ni^{III}L,HQ]^+$ or $[Ni^{III}L,HZ]^+$ species. Further electron transfer within this solvent cage to give nickel(II) and the quinone is indistinguishable from a two-electron transfer and does not take place since nickel(III) is produced quantitatively. Instead, the products diffuse apart and either reaction (19) or the disproportionation

$$[Ni^{IV}L]^{2+} + HQ^{\cdot} \text{ or } HZ^{\cdot} \longrightarrow [Ni^{III}L]^+ + Q' \text{ or } Z' + H^+ \quad (19)$$

$$2HQ^{\cdot} \longrightarrow H_2Q + Q' \quad (20)$$

$$2HZ^{\cdot} \longrightarrow H_2Z + Z' \quad (21)$$

reactions (20) and (21) take place. Pulse-radiolysis studies [15] have shown that organic radicals react very rapidly, close to the diffusion limit with $[Ni^{IV}L]^{2+}$ but somewhat slower with $[Ni^{III}L]^{+}$.

Both organic radicals have pK_a values in the range of study; 4.0 for $HQ^{\cdot}$ and 5.0 for $HZ^{\cdot}$.[16] The disproportionation rate is markedly accelerated in the protonated species with a rate for $HQ^{\cdot}$ of 1.2×10^9 dm^3 mol^{-1} s^{-1} at pH 2.6 and for $Q^{\cdot-}$ of 5.5×10^7 dm^3 mol^{-1} s^{-1} at pH 9.2.[17] The second protonation of the radicals giving $H_2Z^{\cdot+}$ and $H_2Q^{\cdot+}$ is estimated to have a pK_a of -1.[18] Thus, at higher pH, oxidation of the deprotonated radical by nickel(III) may be competitive with disproportionation. Unfortunately, the nickel(III) complex is also deactivated on deprotonation with a pK_h of 4.05. No evidence for a 'two-electron transfer,' a monophasic reduction of nickel(IV) was detected at higher pH.

Nature of the Electron Transfers.—Substitution of ligands in the inner-sphere of nickel(IV) is very slow indeed. The complexes are kinetically inert in concentrated HNO_3 and can be optically resolved. Thus it seems likely that the electron-transfer reactions of $[Ni^{VI}L]^{2+}$ proceed by outer-sphere mechanisms. In principle, the rates of these reactions should be amenable to calculation using the Marcus expression (22)

$$\Delta G_{12}^{\ddagger\ddagger} = \tfrac{1}{2}[\Delta G_{11}^{\ddagger\ddagger} + \Delta G_{22}^{\ddagger\ddagger} + \Delta G_r^{\ominus}(1 + \alpha^{\ddagger\ddagger})] \qquad (22)$$

where $\Delta G_{12}^{\ddagger\ddagger}$ is the electrostatics-corrected activation free energy of the cross reaction, $\Delta G_{11}^{\ddagger\ddagger}$ and $\Delta G_{22}^{\ddagger\ddagger}$ are electrostatics-corrected self-exchange rates for the reactants, and $\Delta G_r^{\ominus}$ is the electrostatics-corrected free-energy change for the reaction. The parameter $\alpha^{\ddagger\ddagger}$ is given by equation (23).

$$\alpha^{\ddagger\ddagger} = \Delta G_r^{\ominus}/4(\Delta G_{11}^{\ddagger\ddagger} + \Delta G_{22}^{\ddagger\ddagger}) \qquad (23)$$

A value of 4×10^4 dm^3 mol^{-1} s^{-1} has been suggested for the self-exchange rate of $[Ni^{IV/III}L]^{2+/+}$ from cross reactions with $[Co(phen)_3]^{2+}$ (phen = 1,10-phenanthroline) and $[Co(edta)]^{2-}$ (edta = ethylenediaminetetra-acetate) giving $\Delta G_{11}^{\ddagger\ddagger}$ a value of 8.73 kcal mol^{-1}. Self-exchange rates for the radical species have been estimated to be 5×10^7 dm^3 mol^{-1} s^{-1} [18] giving $\Delta G_{22}^{\ddagger\ddagger}$ a value of 4.50 kcal mol^{-1}. The reduction potentials of the radicals $HQ^{\cdot}$ and $HZ^{\cdot}$ are 0.48 and 0.50 V respectively based on the experimental potentials for the radical anions,[19,20] the pK_a values for the radicals given previously, and pK_a values of 11.4 for HQ^-/Q^{2-} [12] and 13.0 for HZ^-/Z^{2-}.[11]

Calculated rate constants for the dominant nickel(IV) reactions are shown in Table 3 and are in very good agreement with the experimental values bearing in mind the large uncertainty in the radical self-exchange rates. If reactions of nickel(IV) and nickel(III) are both outer-sphere in nature, then the ratio of the rate constants for similarly charged ions $k[Ni^{III}(HL)]^{2+}/[Nik^{IV}L]^{2+}$ should be constant irrespective of the reductant. This ratio varies from 0.5 to 2.2 in the present work, smaller than the range 10—4 found with reactions which are most likely to be outer-sphere in nature.[4,21] An order of magnitude difference in this parameter is difficult to reconcile on the basis of an exclusive outer-sphere mechanism for both reagents and it is likely that the nickel(III) complexes, in this instance, show some inner-sphere character.

No indication of the rate of substitution of the complexes $[Ni^{III}(HL)]^{2+}$ and $[Ni^{III}L]^{+}$ is available but addition of CN^- and H_2edta^{2-} to solutions of $[Ni^{III}L]^{+}$ accelerate decomposition although the process is not comparable in rate with reduction by HZ^- or HQ^-. However, exchange at only one co-ordination position is required for reaction with reductants which have substituents capable of co-ordination to the metal ion and axial substitution in tetragonal nickel(III) complexes is known to be rapid ($>10^6$ dm^3 mol^{-1} s^{-1}) while equatorial substitution is sluggish.[22] It is proposed that a Ni–N(oxime) bond is broken to facilitate electron transfer. This should be easier when the oxime is protonated and might explain the greater reactivity of $[Ni^{III}(HL)]^{2+}$ over $[Ni^{III}L]^{+}$ although other factors such as the respective reduction potentials may be equally important.

An inner-sphere mechanism is also supported by Marcus calculations. Estimates of the $[Ni^{III/II}L]^{+/0}$ and $[Ni^{III/II}(HL)]^{2+/+}$ self-exchange rates are 3×10^3 and 9×10^2 dm^3 mol^{-1} s^{-1} respectively, calculated from the cross reactions with $[Co(phen)_3]^{2+}$ and other outer-sphere reagents. These give calculated rates with HQ^- and HZ^- which are approximately two orders of magnitude lower than experimentally determined. Similar conclusions can be drawn from the ascorbate data where the reduction potential and self-exchange rate of the radical have been estimated.

Other Studies.—During the course of the preparation of this paper, a paper dealing with the kinetics and mechanism of the reduction of the nickel(IV) complex by 1,2- and 1,4-dihydroxybenzene was communicated to the authors.[23] The mechanistic treatment is similar except that the reaction at low pH is treated as the rate-determining monophasic reduction of nickel(IV) and consequently this leads to some inaccuracy in determining the rate constants in acidic media. These rate data are presented in Table 3 and can be seen to be in substantial agreement with those obtained in the present work.

Thallium(III) *Oxidation of Nickel*(II).—Reaction of the nickel(II) complex $[Ni(H_2L)]^{2+}$ with thallium(III) in perchlorate media is slow, complex, and was not examined in great detail. However, when a solution containing 1.0×10^{-4} mol dm^{-3} Tl^{III} and 2.0×10^{-4} mol dm^{-3} $[Ni(H_2L)]^{2+}$ was allowed to react at pH 6.0, the resulting oxidized nickel species was identified solely as nickel(IV).* No trace of nickel(III) was detected. Under the conditions of the study, formation of nickel(III) by nickel(II) reduction of nickel(IV) is thermodynamically favourable but is slow enough not to interfere with the study.[21] Comparable oxidations of nickel(II) with one-electron oxidants produce exclusively, nickel(III). Thus it appears that the thallium(III) oxidation of nickel(II) proceeds in a single two-electron step.

This change in mechanism to an apparent single, two-electron process may be ascribed to two sources. Thallium(II) is much more reactive ($E^{\ominus}$ $Tl^{2+/+} = 2.22$ V) [24] than semiquinone type radicals and hence the activation energy for the one-electron oxidation of nickel(II) will be substantial. Pathways involving two-electron transfer will be preferred. In the present case, such a pathway might be facilitated by an inner-sphere interaction. Both nickel(II) and thallium(III) are relatively labile and the formation of an inner-sphere complex in which the oxime oxygen of the nickel complex is substituted into the inner co-ordination sphere of the thallium(III) is a possibility. Clearly, this reaction deserves more detailed study.

Conclusions

The reduction of $[Ni^{IV}L]^{2+}$ by 1,2- and 1,4-dihydroxybenzene proceeds, like the ascorbate reduction, in two one-electron steps. In contrast, oxidation of nickel(II) by thallium(III) is a two-electron process. While reactions of nickel(IV) are outer-sphere in nature, those of nickel(III) are likely to proceed by an inner-sphere mechanism. The ratio $k_{[Ni^{IV}L]^{2+}}/k_{[Ni^{III}(HL)]^{2+}}$ has been used as a useful parameter in establishing the nature of the electron-transfer process.

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* This identification is facilitated by quenching the reaction in 2 mol dm^{-3} $HClO_4$. Disproportionation of any nickel(III) formed is slow ($t_{\frac{1}{2}} \sim 3$ min).

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