Kinetics and Mechanisms of Reduction of a Nickel(IV) Complex by Ascorbate Ion

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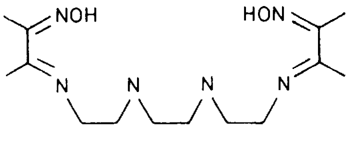
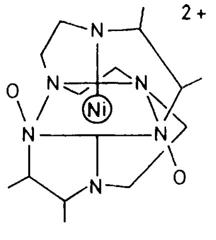
The kinetics of reduction of a nickel(IV) oxime complex by ascorbate ion to give the corresponding nickel(II) species are reported. Ascorbate ion is the sole reductant with second-order rate constants 3.02×10^5 dm^3 mol^{-1} s^{-1} and 1.36×10^4 dm^3 mol^{-1} s^{-1} for reactions with protonated and unprotonated forms of the oxidant respectively at 25.0 °C and 0.10 mol dm^{-3} ionic strength. The origin of the protonation of nickel(IV), pK_h 3.70, is discussed. Electron spin resonance experiments suggest that the redox mechanism involves two discrete one-electron transfer steps with formation of a nickel(III)–oxime intermediate. The first step in the reduction goes by an outer-sphere pathway and a self-exchange rate around 10^4 dm^3 mol^{-1} s^{-1} is calculated for the Ni^{IV}–Ni^{III} couple. Studies with optically active solutions of nickel(IV) show no chiral discrimination in the reaction.

THERE is considerable interest in the chemistry of unusual oxidation states for first-row transition-metal elements in aqueous solution.[1] The most common oxidation state for nickel is Ni^{2+} and although a considerable amount is known [2] about Ni^{3+}, Ni^{4+} has been less well studied. A number of complexes containing nickel, formally in its tetravalent state, have been reported,[1,3] but many of these are best described as complexes of the divalent ion with oxidised forms of the ligands. However, complexes with oxime ligands allow oxidation at the metal centre, certainly as far as the trivalent level, and have reasonable lifetimes in aqueous solution. The compound with the sexidentate ligand 3,14-dimethyl-4,7,10,13-tetra-azahexadeca-3,13-diene-2,15-dione dioxime, H$_2$L, (I), has pseudo-octahedral co-ordination, (II), and forms with the loss of two oxime protons. It is substitution inert even in strongly acidic media [4,5] and can be optically resolved [6] consistent with the low-spin d^6 electronic configuration of nickel(IV).



(I)



(II)

The nickel(IV) complex, [NiL]$^{2+}$, undergoes [5] a single reversible two-electron reduction at pH < 5, (1), with a potential of 0.95 V (*vs.* n.h.e., normal hydrogen electrode)

$$[\mathrm{NiL}]^{2+} + 2\mathrm{H}^+ + 2\mathrm{e}^- \rightleftharpoons [\mathrm{Ni(H_2L)}]^{2+} \qquad (1)$$

while above this pH the intermediate trivalent state can be detected. Relevant potentials are 0.66 V for (2),

$$[\mathrm{NiL}]^{2+} + \mathrm{e}^- \rightleftharpoons [\mathrm{NiL}]^+ \qquad (2)$$

0.39 V for (3), and 0.87 V for (4), all at 25 °C and 0.10 mol dm^{-3} ionic strength. The low substitution lability

$$[\mathrm{NiL}]^+ + \mathrm{e}^- \rightleftharpoons [\mathrm{NiL}] \qquad (3)$$

$$[\mathrm{NiL}]^+ + \mathrm{H}^+ + \mathrm{e}^- \rightleftharpoons [\mathrm{Ni(HL)}]^+ \qquad (4)$$

and high reduction potential of [NiL]$^{2+}$ are likely to result in outer-sphere electron-transfer mechanisms. Since, unlike the corresponding platinum(IV)–platinum(II) couple, no major geometry change is expected in the reduction of nickel(IV) to nickel(II), there is a possibility, albeit remote, of an outer-sphere two-electron transfer. L-Ascorbic acid, H$_2$A, is a well studied reductant with a two-electron potential [7] of 0.41 V at 25 °C and 0.10 mol dm^{-3} ionic strength, (5). Acidity constants (pK_a) of 4.03 and 11.3 are also reported.[8]

$$\mathrm{A'} + 2\mathrm{H}^+ + 2\mathrm{e}^- \rightleftharpoons \mathrm{H_2A} \qquad (5)$$

In this paper, the kinetics and mechanisms of reduction of nickel(IV) by L-ascorbic acid over the pH range 1—6 are presented.

EXPERIMENTAL

The nickel(II) and nickel(IV) complexes with (I) were obtained as the perchlorate salts by methods outlined by Chakravorty and co-workers.[4] Analytical data were satisfactory {Found: C, 28.9; H, 4.30; N, 14.7. Calc. for [NiL][ClO$_4$]$_2$: C, 29.6; H, 4.60; N, 14.8%. Found: C, 30.05; H, 4.55; N, 14.6. Calc. for [Ni(H$_2$L)][ClO$_4$]$_2$: C, 29.5; H, 4.9; N, 14.7%}. Solutions of nickel(IV) were standardised spectrophotometrically using literature absorption coefficients,[4] λ/nm (ε/dm^{-3} mol^{-1} cm^{-1}), 500 (6 300), 430 (5 960). Partial optical resolution of the nickel(IV) complex was achieved using a cation-exchange method outlined previously.[6] The partially resolved complexes in chiral buffers were readsorbed on SP Sephadex cation-exchange resin and washed with copious amounts of distilled water. After suction drying, the partially resolved complex was eluted with 1.0 mol dm^{-3} Na[ClO$_4$]. L-Ascorbic acid (B.D.H.) and sodium acetate (B.D.H., AnalaR) were used. All other reagents were of AnalaR quality.

Kinetic measurements were made in 1.0 × 10^{-2} mol dm^{-3} acetate buffer at an ionic strength of 0.10 mol dm^{-3} ($Na[ClO_4]$) unless otherwise stated. All solutions were prepared immediately prior to use and were bubbled with chromium(II) scrubbed nitrogen gas for at least 15 min to prevent aerial oxidation of ascorbic acid. The nickel(IV) complex decomposes slowly at room temperature and hence all kinetic experiments were run under pseudo-first-order conditions with an excess of ascorbate ion ($[NiL^{2+}]_T$ 0.5 × 10^{-5}—1.0 × 10^{-5} mol dm^{-3}; $[H_2A]_T$ 8 × 10^{-5}—200 × 10^{-5} mol dm^{-3}). The pH was varied from 1 to 6 and was determined immediately after reaction using an E.I.L. 7055 pH meter. A saturated calomel (KCl) reference electrode was used and hydrogen-ion concentrations were evaluated using the relationship $-\log[H^+] = pH - 0.11$.[9]

Reactions were monitored at the absorption maximum of the nickel(IV) complex at 500 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 good first-order behaviour, (6), under the above conditions. Observed rate

$$-d[Ni^{IV}]/dt = k_{obs.}[Ni^{IV}] \quad (6)$$

constants, $k_{obs.}$, were evaluated by least-squares analysis using a Data General Nova 2 minicomputer. At least three rate determinations were made for each experiment. Linear regression techniques, weighting $k_{obs.}^{-1}$ where appropriate, were employed for data analysis.

The reaction stoicheiometry was determined by the addition of aliquots of ascorbic acid solution to a standard nickel(IV) solution which was then restandardised. Electron spin resonance spectra were obtained at 125 K using a JEOL JES-FE1X *X*-band instrument and at room temperature using a Decca X3 spectrometer with a Newport Instruments 27.9-cm magnet system. Solutions containing the nickel(IV) complex (*ca.* 10^{-4} mol dm^{-3}, pH 4.5) were mixed at 0 °C with aliquots of ascorbic acid solution and quenched in liquid nitrogen within a few seconds.

RESULTS

The results of the experiments to determine the stoicheiometry of the reaction between nickel(IV) and ascorbic acid, Table 1, indicate that one mole of ascorbic acid will react with one mole of the nickel(IV) complex, (7). This is consistent with the formation of dehydroascorbate, A′, and nickel(II) as reaction products.

TABLE 1

Stoicheiometry of the reaction between $[NiL]^{2+}$ and HA^-

Amount of reagent added/mmol		Amount $[NiL]^{2+}$ remaining/ mmol	$[NiL]^{2+}/HA^-$
$[NiL]^{2+}$	HA^-		
5.45	0.88	4.36	0.93
4.91	1.31	3.44	1.12
4.36	1.75	2.60	1.01
3.82	2.19	1.56	1.03
3.27	2.63	0.66	0.99
		Average	1.01 ± 0.11

$$[NiL]^{2+} + H_2A \longrightarrow [Ni(H_2L)]^{2+} + A' \quad (7)$$

A list of observed pseudo-first-order rate constants obtained under various conditions for the reduction of nickel(IV) is given in Table 2. The rate shows a first-order dependence on total ascorbic acid concentration, $[H_2A]_T$, with a second-order rate constant 2.65 ± 0.01 × 10^4 dm^3 mol^{-1} s^{-1} and a very small intercept 0.66 ± 0.82 s^{-1} at pH 3.24 ± 0.04. However, the second-order rate constants, k_{s0}, have a strong and complex dependence on pH, Figure 1. This bell-shaped dependence suggests that two protonation effects are involved in governing the reaction rate.

TABLE 2

Pseudo-first-order rate constants for the reduction of $[NiL]^{2+}$ by ascorbate ion at 25 °C and 0.10 mol dm^{-3} ($[Na[ClO_4]]$) ionic strength [a]

$-\log[H^+]$	$10^2[acetate]_T$/ mol dm^{-3}	$10^4[ascorbate]_T$/ mol dm^{-3}	$k_{obs.}/s^{-1}$
1.00	1.00	5.11	0.15 ± 0.01
1.30	1.00	5.11	0.28 ± 0.03
1.89	1.00	5.11	1.08 ± 0.02
2.25	1.00	5.11	2.44 ± 0.28
2.78	1.00	5.11	7.25 ± 0.16
3.15	1.00	0.82	2.51 ± 0.08
3.16	1.00	2.06	6.16 ± 0.06
3.15	1.00	4.12	12.6 ± 0.2
3.14	1.00	8.24	24.4 ± 0.4
3.12	1.00	12.4	34.2 ± 2.8
3.09	1.00	16.5	45.5 ± 8.8
3.07	1.00	20.6	51.8 ± 7.1
3.27	1.00	5.11	16.5 ± 0.2
3.78	1.00	5.11	25.3 ± 1.8
4.11	1.00	5.11	28.6 ± 1.0
4.55	1.00	5.11	20.1 ± 5.2
5.27	0.50	5.02	9.78 ± 0.06
5.29	1.00	5.02	9.41 ± 0.16
5.29	2.50	5.02	9.77 ± 0.08
5.29	5.00	5.02	9.37 ± 0.12
5.33	1.00	5.11	9.25 ± 0.38
5.35	0.10	5.02	9.89 ± 0.50
5.67	1.00 [b]	5.47	8.25 ± 0.23
3.02 [c]	10.0	16.8	20.2 ± 0.1
3.02 [d]	10.0	16.8	20.6 ± 0.4

[a] $[NiL^{2+}]$ = 5 × 10^{-6}—10 × 10^{-6} mol dm^{-3}. [b] $[edta]_T$ = 2.23 × 10^{-4} mol dm^{-3} = total concentration of ethylenediaminetetra-acetate species. [c] Ionic strength 1.0 mol dm^{-3} first eluted optically active nickel(IV) fraction. [d] Ionic strength 1.0 mol dm^{-3} second eluted optically active nickel(IV) fraction.

One of the reactants, ascorbic acid, is known to show protonation behaviour, (8), in the pH range examined with a

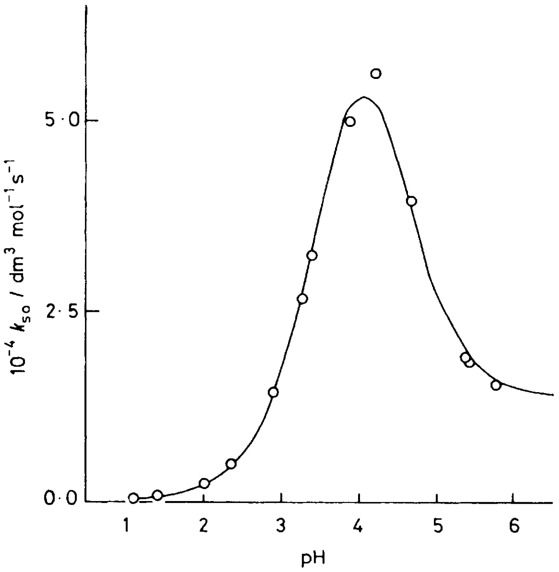


FIGURE 1 The dependence of second-order rate constant k_{s0} on pH for the reduction of nickel(IV) by ascorbic acid at 25.0 °C and 0.10 mol dm^{-3} ionic strength

pK_a of 4.03. In general,[10,11] the reactivity of the ascorbate ion with inorganic oxidants exceeds that of ascorbic acid

$$H_2A \rightleftharpoons H^+ + HA^- \qquad (8)$$

and this was considered the most likely source of the increase in reaction rate with pH at low pH. Below pH 2.5, a plot of k_{so} against $[H^+]^{-1}$ is linear with slope $3.75 \pm 0.02 \times 10^{-2}$ s^{-1} and a slightly negative intercept -0.82 ± 0.88 dm^3 mol^{-1} s^{-1}, zero within experimental error, consistent with ascorbate ion as the sole, active reductant. Second-order rate constants were corrected for ascorbate ion using the relationship (9) where K_a is 9.33×10^{-5} mol dm^{-3}. The

$$k_{so}' = k_{so}K_a/([H^+] + K_a) \qquad (9)$$

second protonation constant, K_h, was evaluated by an iterative least-squares procedure using expression (10) where k_a and k_b are respectively the limiting rate constants for

$$k_{so}' = k_b + (k_a - k_b)\{[H^+]/([H^+] + K_h)\} \qquad (10)$$

reactions of ascorbate ion in acidic and basic solutions. The best-fit values give $K_h = 1.99 \pm 0.08 \times 10^{-4}$ mol dm^{-3}, $k_a = 3.02 \pm 0.09 \times 10^5$ dm^3 mol^{-1} s^{-1}, and $k_b = 1.36 \pm 0.35 \times 10^4$ dm^3 mol^{-1} s^{-1} and yield the calculated curve shown in Figure 1.

The nickel(IV) complex has no reported protonation around pH 4 and so experiments designed to test for the effects of buffer (pK_a 4.50) [8] and trace metal-ion catalysis on the reaction rate were also carried out. In the first of these, the total acetate concentration was varied from 5.0×10^{-2} to 1.0×10^{-3} mol dm^{-3} with minimal effect on the rate constant, Table 2. This effectively rules out outer-sphere complexation by acetate as an explanation for the decrease in reaction rate with pH above pH 4 and precludes appreciable general-acid catalysis. Addition of ethylenediaminetetra-acetic acid (2.23×10^{-4} mol dm^{-3}) to the reaction mixture also produced no significant effects. Thus it seems likely that protonation of the nickel(IV) complex takes place without a marked effect on the reduction potential.

Reactions of partially optically resolved solutions of nickel(IV) with L-ascorbic acid showed little or no chiral discrimination in their reactions. The differences in rate for the two reagents were within experimental error.

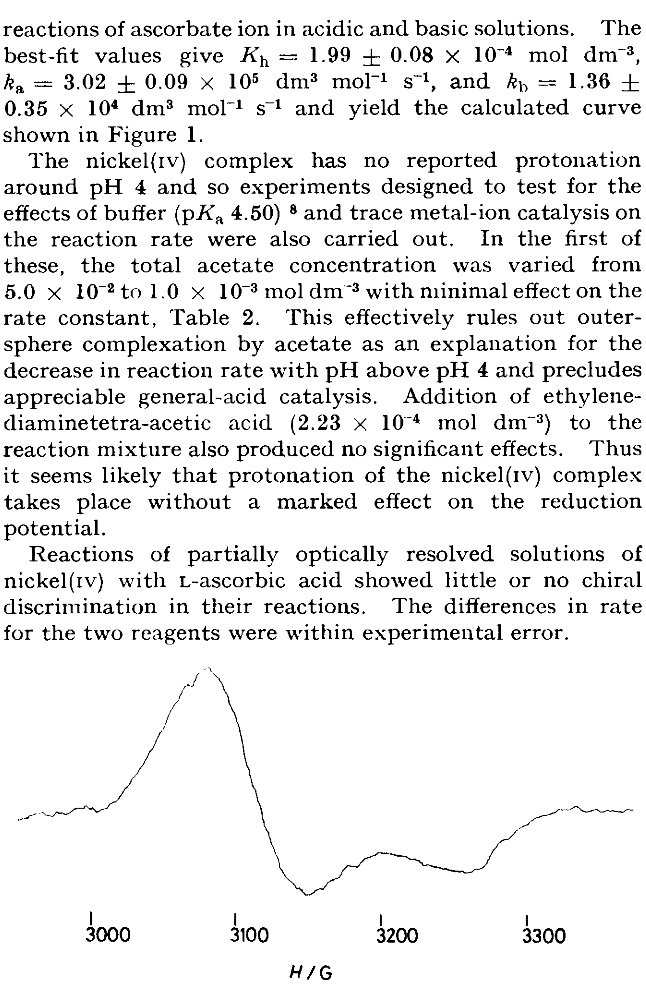


FIGURE 2 Electron spin resonance spectrum of the nickel(III) impurity, $[Ni(HL)]^{2+}$, in a crystalline sample of $[NiL][ClO_4]_2$ at room temperature. The microwave frequency is 9 270 MHz

Electron spin resonance spectra of crystalline samples of the nickel(IV) complex $[NiL][ClO_4]_2$ showed a weak signal (<1%), Figure 2, indicating contamination by a paramagnetic impurity. The spectrum is, to a first approximation, axial with $g_\perp = 2.155 \pm 0.001$ and $g_\parallel = 2.033 \pm 0.001$ as might be expected for a nickel(III) complex.[12] The signal persists, but to a much lesser intensity ($<10^{-6}$ mol dm^{-3}), in aqueous glasses formed by quenching solutions of nickel(IV). Addition of ascorbate to nickel(IV) solutions at 0 °C resulted in an increase in the nickel(III) signal by *ca.* 60% over comparable solutions containing nickel(IV) alone. In the mixed solutions, the deep red nickel(IV) colour had visibly decayed.

DISCUSSION

The reaction stoicheiometry, (7), indicates that overall, two electrons are transferred from ascorbic acid to nickel(IV) to give nickel(II) and dehydroascorbate. First-order rate dependences on $[NiL^{2+}]_T$ and $[H_2A]_T$ provide no kinetic evidence for reaction intermediates and the rate-determining step must involve either (*a*) simultaneous transfer of both electrons with direct formation of nickel(II) from nickel(IV) or (*b*) single electron transfer with formation of a transient nickel(III) intermediate followed by rapid reduction of the nickel(III).

Electron spin resonance experiments indicate the presence of a paramagnetic trace species in solutions of nickel(IV) which is considerably enhanced on addition of ascorbic acid, even when the nickel(IV) colouration has visibly decayed. The magnetic parameters are consistent with a nickel(III) complex.[12] Although somewhat ambiguous, this result lends support to mechanism (*b*) and participation of a nickel(III) intermediate in the reaction.

The potential of the Ni^{3+}–Ni^{2+} couple is larger than that of Ni^{4+}–Ni^{3+} and it is expected that nickel(III) will react faster with ascorbate than would nickel(IV). It could thus be argued that nickel(III) must be produced in the ascorbate reduction of nickel(IV). No evidence was found for an ascorbate radical.

The paramagnetic intermediate has an average g value of 2.114 which shows a significant contribution to paramagnetism and is consistent [12,13] with trivalent nickel. The complex has tetragonal geometry with the unpaired electron in a d_{z^2} orbital. A report [5] of the nickel(III) complex isolated from oxidation of $[Ni(H_2L)]^{2+}$ with peroxodisulphate gives values $g_\perp = 2.16$ and $g_\parallel = 2.04$ similar to those reported in the present work. It is likely that both complexes are the same and the previous workers suggested that the complex could be formulated as $[Ni(HL)]^{2+}$ Protonation of the oxime groups on $[NiL]^+$ has not been detected above pH 5 [5] and although protonation is not observed [14] in the corresponding iron(III) complex above pH 1, protonated forms of the cobalt(III) complex have been reported.[15]

No estimate of the ligand-exchange rate of $[NiL]^{2+}$ is available but it must be extremely slow in common with other octahedral low-spin d^6 ions. Optically active solutions of nickel(IV) can be kept for several days before decomposition without racemisation.[6] Redox reactions on the millisecond to second time scale are thus likely to be outer sphere in nature.

Two protic equilibria are required to explain the pH dependence of the reaction rate. However, only one of the reactants, ascorbic acid, has been shown [8] to have a pK_a in the range examined. The protonations of the oxime groups on the nickel(IV) complex, $[NiL]^{2+}$, are expected at lower pH values than those for $[NiL]^+$ and have not been detected [5] above pH 1. Indeed the visible spectrum of the complex remains substantially unchanged over the range pH 1—6. Buffer effects and the effects of trace metal-ion catalysis, a problem frequently encountered in the outer-sphere oxidation of organic substrates,[16] cannot explain the protonation at pK_h 3.70. One further possibility examined, that reduction of nickel(IV) occurs within the time of mixing of the stopped-flow apparatus and that the reaction monitored involves some subsequent intermediate, for example $[NiL]^+$, was resolved by a point-by-point spectrum of the absorbance change, Figure 3. This shows the characteristic two-peaked curve of nickel(IV).

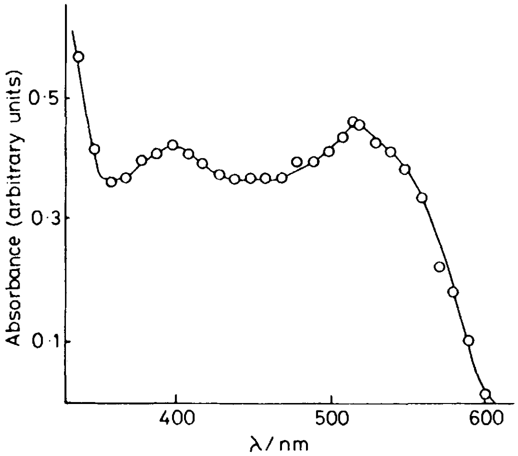


FIGURE 3 Point-by-point spectrum of the absorbance change in the reaction between nickel(IV) (3.6×10^{-5} mol dm^{-3}) and ascorbic acid (5.6×10^{-4} mol dm^{-3}) at pH 5.88 in 1.0×10^{-2} mol dm^{-3} acetate buffer, 0.10 mol dm^{-3} ionic strength ($Na[ClO_4]$) and at 25.0 °C

It is concluded that the protic equilibrium involves $[NiL]^{2+}$ with pK_h 3.70, (11). The absence of an acid-independent

$$[Ni(H\cdots L)]^{3+} \rightleftharpoons [NiL]^{2+} + H^+ \qquad (11)$$

rate at low pH is consistent with the ascorbate ion, HA^-, as the sole active reductant and a complete reaction scheme [(12)—(15)] is presented. There are a number

$$[Ni(H\cdots L)]^{3+} + HA^- \xrightarrow{k_a} [Ni(HL)]^{2+} + HA^{\bullet} \qquad (12)$$

$$[NiL]^{2+} + HA^- \xrightarrow{k_b} [NiL]^+ + HA^{\bullet} \qquad (13)$$

$$[Ni(HL)]^{2+} \rightleftharpoons [NiL]^+ + H^+ \qquad (14)$$

$$[Ni(HL)]^{2+} + HA^{\bullet} \longrightarrow [Ni(H_2L)]^{2+} + A' \qquad (15)$$

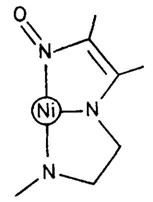
of alternatives to (14) and (15) which are rapid and take place after the rate-determining step. Best-fit parameters to the rate law (16) are $k_a = 3.02 \times 10^5$ dm^3 mol^{-1} s^{-1} and $k_b = 1.36 \times 10^4$ dm^3 mol^{-1} s^{-1} using $K_a = 9.33 \times 10^{-5}$ mol dm^{-3} and $K_h = 1.99 \times 10^{-4}$ mol dm^{-3}.

The greatly increased reactivity of ascorbate ion over ascorbic acid is in good agreement with the behaviour of these reductants to other one-electron outer-sphere oxidants.[10,11]

$$-d[NiL^{2+}]_T/dt = \left\{\frac{K_a k_a[H^+] + K_a K_h k_b}{K_a K_h + (K_a + K_h)[H^+] + [H^+]^2}\right\} [H_2A]_T[NiL^{2+}]_T \qquad (16)$$

This reflects the ease of oxidation of H_2A and HA^- and the application of Marcus theory to a number of one-electron outer-sphere redox reactions has led [11] to values around 0.93 V and 1.35 V for the one-electron potentials $HA^{\bullet}$–HA^- and $H_2A^{\bullet +}$–H_2A respectively, assuming self-exchange rate constants between 10^7 and 10^9 dm^3 mol^{-1} s^{-1}. Using these values, the self-exchange rate for the $[NiL]^{2+}$–$[NiL]^+$ couple is calculated to be between 10^3 and 10^5 dm^3 mol^{-1} s^{-1}, although experiments [17] with $[Co(phen)_3]^{2+}$ (phen = 1,10-phenanthroline) as reductant indicate a much smaller value of *ca.* 1 dm^3 mol^{-1} s^{-1} and discussion of this topic will be the subject of a further publication.[17]

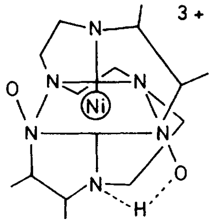
The nature of the protonation of the nickel(IV) complex, $[NiL]^{2+}$, requires some comment. Results of cyclic voltammetry experiments show clearly that the protonation with pK_h 3.70 does not involve the oxime protons. These oxime protons become more acidic as the oxidation state of the metal ion in the complex increases. Thus for [NiL], protons are added with pK_a values 7.80 and 5.90, while for $[NiL]^+$, protonation occurs at pH < 5, and for $[NiL]^{2+}$, below pH 1. The deprotonated oxime–imine chromophore provides considerable stabilisation of higher oxidation states and can be represented as a strong N^- chromophore, (III). Protonation will considerably weaken the imine nitrogen–metal bond and will destabilise the higher oxidation state as revealed by the appropriate reduction potentials. Protonation on the nickel(IV) complex might thus be expected to facilitate electron transfer yielding protonated nickel(III).



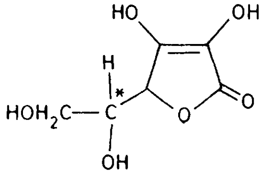
(III)

The situation is very similar to metal–N peptide bond formation where, if the metal ion is substitution inert, ' outside ' protonation can occur as a kinetic intermediate before metal–N peptide rupture takes place.[18] This ' outside ' protonation has been shown [19,20] to enhance the redox reactivity of copper(III)–peptide complexes. The protonation of $[NiL]^{2+}$ is considered to involve a hydrogen-bonded intermediate, (IV), in which metal–N imide bonding is not substantially weakened.

Finally, the reaction shows no stereospecificity when different optical isomers are used. This may indicate that precursor complex formation is weak. On the other hand, the chiral centre in the ascorbate ion is far removed from the site of oxidation, (V), and may not come in close proximity to the nickel(IV) complex.



(IV)



(V)

Chiral discrimination with nickel(IV) has been noted with other reductants.[6]

Conclusions.—The two-electron reduction of $[NiL]^{2+}$ to $[Ni(H_2L)]^{2+}$ by ascorbic acid proceeds by two discrete single-electron-transfer steps. The first of these is outer sphere in nature and results in formation of a paramagnetic nickel(III) intermediate, $[Ni(HL)]^{2+}$. Ascorbate ion is the active reducing species and 'outside' protonation, with pK_h 3.70, enhances the reactivity of the nickel(IV) complex. No chiral discrimination is noted in the reaction.

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