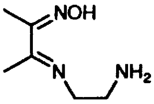
Kinetic Studies on the Reduction of Nickel(IV) and Nickel(III) Oxime–Imine Complexes by Ascorbic Acid†

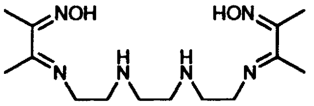
Basudeb Saha, Sumana Gangopadhyay, Mahammad Ali and Pradyot Banerjee*
Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700032, India

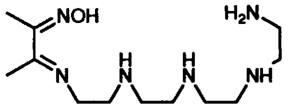
The oxidation of ascorbic acid by $[Ni^{III}L^1]^{2+}$ and $[Ni^{IV}L^3_2]^{2+}$ complexes (where HL^1 = 15-amino-3-methyl-4,7,10,13-tetraazapentadec-3-en-2-one oxime and HL^3 = 6-amino-3-methyl-4-azahex-3-en-2-one oxime) has been investigated by stopped-flow spectrophotometry in the range pH 2.50–8.20, with I = 0.20 mol dm^{-3} $NaClO_4$ and T = 30 °C, using variable concentrations of ascorbic acid. At a particular pH both the reactions are second order, first order with respect to ascorbic acid and the complexes, and follow the general rate law $-1/m\ d[NiL_x^{n+}]/dt = k[NiL_x^{n+}][H_2A]_T$ where H_2A = ascorbic acid and m represents the stoichiometric factor (m = 2 for $[Ni^{III}L^1]^{2+}$ and 1 for $[Ni^{IV}L^3_2]^{2+}$). In the reduction of $[Ni^{IV}L^3_2]^{2+}$, the monophasic reaction traces throughout the experimental pH range (2.50–8.20) imply the involvement of nickel(III) complexes in the rate-determining step. A detailed evaluation of the reduction was achieved by considering suitable pH regions and employing appropriate computer programs to fit the experimental data. Application of the Marcus theory in calculating the theoretical rate constants and a comparison of these constants with the respective experimental values reveals the occurrence of an outer-sphere mechanism for the oxidation of A^{2-} by both $[Ni^{III}L^1]^{2+}$ and $[Ni^{IV}L^3_2]^{2+}$ as well as by $[Ni^{III}L^2]^+$ where H_2L^2 = 3,14-dimethyl-4,7,10,13-tetraazahexadec-3,13-diene-2,15-dione dioxime. The oxidation of H_2A and HA^- seems to follow a concerted electron–proton transfer with initial association of the reactants.

The chemistry of unusual oxidation states of nickel is a subject of continuing interest.[1] Perhaps the most widely acclaimed chelates used to stabilise nickel-(IV) and -(III) states are the oxime[2–5] and oxime–imine ligands[6–10] HL^1–HL^3 through strong L ⟶ M σ donation.

Previous studies have established that HL^1 (15-amino-3-methyl-4,7,10,13-tetraazapentadec-3-en-2-one oxime) can stabilise nickel(III)[11] whereas both HL^3 (6-amino-3-methyl-4-azahex-3-en-2-one oxime and H_2L^2 (3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime) stabilise the nickel(IV)[8–10] oxidation state. It is also significant in this context that (*i*) the nickel(IV) complexes derived from H_2L^2 and HL^3 contain two oximato groups per nickel atom and (*ii*) HL^1, with one oxime function, is unable to facilitate the oxidation of nickel(II) to nickel(IV) although the nickel(III) species is readily formed. Despite the occurrence of several nickel-(IV) and -(III) complexes, there is little known about chemical electron transfer involving these complexes with biologically relevant molecules. Lappin *et al.*[12] carried out kinetic studies on the oxidation of ascorbic acid by $[Ni^{IV}L^2]^{2+}$. The pH-rate profile showed a bell-shaped curve, and the kinetic data were interpreted by considering the protonation of $[Ni^{IV}L^2]^{2+}$ with a pK_h value of 3.70. In a subsequent communication the same authors[13] reinterpreted the kinetic results by envoking the nickel(III) species as the sole oxidant, and the strong pH rate dependence was argued to arise from the protonation of the nickel(III) complex with pK_h 4.03. We present here a kinetic study on the oxidation of ascorbic acid by $[Ni^{IV}L^3_2]^{2+}$ and $[Ni^{III}L^1]^{2+}$ which are significant because of their comparable electron-transfer properties, as evidenced from electrochemical studies, and it can shed light on the mechanistic consequences of changes in the degree of protonation upon electron transfer.


HL^3


H_2L^2


HL^1

Experimental

Synthesis of Nickel Complexes.—(*15-Amino-3-methyl-4,7,10,13-tetraazapentadec-3-en-2-one oximato*)*nickel*(III) *perchlorate*, $[NiL^1][ClO_4]_2$. The nickel-(II) and -(III) complexes of HL^1 were obtained as the perchlorate salts by the method outlined by Singh and Chakravorty[11] (Found: C, 27.15; H, 5.35; N, 15.90. Calc. for $C_{12}H_{28}Cl_2N_6NiO_9$: C, 27.25; H, 5.45; N, 16.0. Found: C, 27.30; H, 5.10; N, 15.85. Calc. for $C_{12}H_{27}Cl_2N_6NiO_9$: C, 27.35; H, 5.30; N, 15.80%). The nickel(II) complex has absorption maxima at 510 (75) and 815 nm (29 dm^3 mol^{-1} cm^{-1}).

Solutions of the nickel(III) complex were standardised spectrophotometrically using the known absorption coefficient at 498 nm [(2.7 ± 0.20) × 10^3 dm^3 mol^{-1} cm^{-1}].

Bis(*6-amino-3-methyl-4-azahex-3-en-2-one oxime*)*nickel*(II) *perchlorate*, $[Ni(HL^3)_2][ClO_4]_2$. The nickel(II) complex of HL^3 was prepared by the literature method[9] and recrystallised from ethanol to yield the pure product (Found: C, 26.70; H, 4.85; N, 15.25. Calc. for $C_{12}H_{26}Cl_2N_6NiO_{10}$: C, 26.65; H, 4.80; N, 15.40%). The corresponding nickel(IV) complex $[Ni^{IV}L^3_2][ClO_4]_2$ was prepared by oxidising the nickel(II) complex with concentrated HNO_3 and was standardised from the UV/VIS spectrum in aqueous solution by com-

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† *Supplementary data available* (No. SUP 57065, 4 pp.): observed rate constants at different [H$^+$]. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

parison with the known absorption coefficients at 505 [(6.1 ± 0.12) × 10^3] and 419 nm [(4.9 ± 0.15) × 10^3 dm^3 mol^{-1} cm^{-1}].

Kinetics.—Materials. Analytical grade ascorbic acid (Wako Pure Chemical, Japan) was used directly without further purification. Doubly recrystallised sodium perchlorate was used to maintain the ionic strength and doubly recrystallised sodium acetate, sodium dihydrogenphosphate and acetic acid and sodium hydroxide (all of reagent grade) were used to maintain the pH of the reaction solutions. All the solutions were freshly prepared prior to the kinetic studies using doubly distilled water.

Measurements. The kinetics under various reaction conditions was monitored by the loss of oxidant measured spectrophotometrically by the stopped-flow technique, using a Union RA-401 stopped-flow spectrophotometer (Otsuka Electronics, Japan) interfaced with a data processor RA-451 (Otsuka Electronics, Japan) comprising a computer (Packard-Bell 286). Conventional plots of $-\log A_t$ *vs.* t were all linear for more than three half-lives indicating a first-order rate dependence on oxidant concentration. The observed rate constants were evaluated by treating the kinetic curve of the average of at least five to six runs by a least-squares curve-fit method. The pseudo-first-order rate constants, k_{obs}, thus evaluated vary within the error limit ±3%. The reaction temperature (±0.1 °C) was controlled by a Haake F3 thermostat by circulating water around the reservoir of the reaction solution. The pH (±0.01) measurements were carried out with a Systronics (model 335, India) pH-meter. Although the measured pH is defined by the activity of the hydrogen ion, the concentration of hydrogen ion in terms of $-\log [H^+]$ for each solution was obtained by calibrating the pH electrode with analytically prepared solutions to the desired ionic strength.

Polymerisation Study.—The oxidation of ascorbic acid by both $[Ni^{III}L^1]^{2+}$ and $[Ni^{IV}L^3{}_2]^{2+}$ complexes, which proceeds through the generation of free radicals, was confirmed by the polymerisation of acrylonitrile, as described earlier.[14]

Stoichiometry and Reaction Products.—The redox stoichiometries were determined at varying concentrations of both the reagent and substrate in each case. The unreacted ascorbic acid and nickel complexes were determined by titrimetric and spectrophotometric techniques respectively. Ratios of 2:1 $[Ni^{III}L^1]^{2+}:[H_2A]_T$ and 1:1 $[Ni^{IV}L^3{}_2]^{2+}:[H_2A]_T$ (where H_2A = ascorbic acid) were found for the oxidation of ascorbic acid by $[Ni^{III}L^1]^{2+}$ and $[Ni^{IV}L^3{}_2]^{2+}$ respectively. Dehydroascorbic acid is the oxidation product of ascorbic acid for both the reactions,[15,16] and was identified by Roe's[16] method after separating the nickel(II) through a cation-exchange column.

Results and Discussion

The oxidation of ascorbic acid by $[Ni^{III}L^1]^{2+}$ and $[Ni^{IV}L^3{}_2]^{2+}$ was conducted under pseudo-first-order conditions with an excess of reagent over the oxidants by observing the disappearance of the nickel complexes at 498 and 505 nm (the absorption maxima) respectively. The kinetic conditions adopted were: $[H_2A]_T$ = (1.0–12.0) × 10^{-4} mol dm^{-3}, $[NiL_x{}^{n+}]$ = 5.0 × 10^{-5} mol dm^{-3} {when $[H_2A]_T$ = (1.0–3.0) × 10^{-4} mol dm^{-3}, $[Ni^{IV}L_x{}^{2+}]$ = 1.0 × 10^{-5} mol dm^{-3}}, pH 2.50–8.20, I = 0.20 mol dm^{-3} NaClO$_4$ and T = 30 °C. At a particular pH plots of k_{obs} *vs.* $[H_2A]_T$ yield a straight line passing through the origin for both the reactions indicating first-order rate dependence on $[H_2A]_T$ and the corresponding results are summarised in Table 1. Thus a general rate law for the oxidation of ascorbic acid by both the nickel complexes is given by equation (1) where m is the stoichiometric factor

$$-1/m\, d[NiL_x{}^{n+}]/dt = k[NiL_x{}^{n+}][H_2A]_T \qquad (1)$$

(m = 2 for $[Ni^{III}L^1]^{2+}$ and 1 for $[Ni^{IV}L^3{}_2]^{2+}$). The effect of the acetate and phosphate buffer was tested within the range [buffer] = (1.0–10.0) × 10^{-2} mol dm^{-3} at a particular pH and was found to be within the limit of experimental error.

Table 1 Pseudo-first-order rate constants for the reduction of $[Ni^{III}L^1]^{2+}$ and $[Ni^{IV}L^3{}_2]^{2+}$ by ascorbic acid at pH 4.0 with $[NiL_x{}^{2+}]$ = 5.0 × 10^{-5} mol dm^{-3}, I = 0.2 mol dm^{-3} NaClO$_4$, $[CH_3CO_2{}^-]$ = 0.02 mol dm^{-3} at 30°C

$[Ni^{III}L^1]^{2+}$		$[Ni^{IV}L^3{}_2]^{2+}$	
10^2 $[H_2A]$/mol dm^{-3}	k_{obs}/s^{-1}	10^2 $[H_2A]$/mol dm^{-3}	k_{obs}/s^{-1}
0.01	1.24	0.01	4.62
0.03	3.12	0.03	20.7
0.05	5.97	0.05	35.9
0.07	8.59	0.07	48.5
0.10	11.04	0.10	64.3
0.12	14.4		66.1

Oxidation of Ascorbic Acid by $[Ni^{III}L^1]^{2+}$.—A spectrophotometric titration at pH 5.0, monitored at 498 nm showed a (2.02 ± 0.03):1 ratio of $[Ni^{III}L^{1\,2+}]:[H_2A]_T$, consistent with equation (2). Over the range pH 5–8, a cyclic voltammogram of

$$2[Ni^{III}L^1]^{2+} + H_2A \longrightarrow 2[Ni^{II}(HL^1)]^{2+} + A^{2-} \qquad (2)$$

$$[Ni^{III}L^1]^{2+} + e^- + H^+ \rightleftharpoons [Ni^{II}(HL^1)]^{2+} \qquad (3)$$

$$[Ni^{II}(HL^1)]^{2+} \xrightleftharpoons{K} [Ni^{II}L^1]^+ + H^+ \qquad (4)$$

$$[Ni^{III}L^1]^{2+} + e^- \rightleftharpoons [Ni^{II}L^1]^+ \qquad (5)$$

$[Ni^{III}L^1]^{2+}$ showed a pH-dependent redox couple [equation (3)] with a formal potential of 0.91 ± 0.02 V *vs.* the normal hydrogen electrode (NHE).[11,17] The nickel(II) complex has a pK value of 6.80[11] [equation (4)] and this, together with $[Ni^{III}L^1]^{2+}$ being a strong acid (pK < 1.0) gives $E°$ = 0.49 V for the couple (5). This potential value is used in the subsequent analysis of the kinetic data.

The oxidation of ascorbic acid by $[Ni^{III}L^1]^{2+}$ has been found to be enormously influenced by the acidity of the reaction medium and was tested in the region pH 2.50–8.00, at $[Ni^{III}L^{1\,2+}]$ = 5.0 × 10^{-5} mol dm^{-3}, $[H_2A]$ = 1 × 10^{-3} mol dm^{-3}, I = 0.20 mol dm^{-3} and T = 30°C. A plot of k (= $k_{obs}/2[H_2A]$, where the number 2 represents the stoichiometric factor) *vs.* $-\log [H^+]$ is shown in Fig. 1(*a*).

The rate dependence on $-\log [H^+]$ can be explained by considering the proton dissociation constants of ascorbic acid (H_2A) [equations (6) and (7)] (since $[Ni^{III}L^1]^{2+}$ is a strong acid

$$H_2A \xrightleftharpoons{K_1} HA^- + H^+ \qquad (6)$$

$$HA^- \xrightleftharpoons{K_2} A^{2-} + H^+ \qquad (7)$$

with pK < 1.0) with reported values pK_1 3.91 and pK_2 11.10[18] at 32.5 °C. In the experimental pH region (2.5–8.0), the reacting species of ascorbic acid likely to be present are H_2A, HA^- and A^{2-} and their reactions can be summarised by equations (8)–(10). The general rate law derived is shown in equation (11).

$$[Ni^{III}L^1]^{2+} + H_2A \xrightarrow{k_0} [Ni^{II}(HL^1)]^{2+} + HA^{\bullet} \qquad (8)$$

$$[Ni^{III}L^1]^{2+} + HA^- \xrightarrow{k_1} [Ni^{II}(HL^1)]^{2+} + A^{\bullet -} \qquad (9)$$

$$[\mathrm{Ni^{III}L^1}]^{2+} + \mathrm{A}^{2-} \xrightarrow{k_2} [\mathrm{Ni^{II}L^1}]^{+} + \mathrm{A}^{\bullet-} \quad (10)$$

$$k = \frac{k_0[\mathrm{H}^+]^2 + k_1K_1[\mathrm{H}^+] + k_2K_1K_2}{[\mathrm{H}^+]^2 + K_1[\mathrm{H}^+] + K_1K_2} \quad (11)$$

In the range pH 2.5–5.5, the k_0 and k_1 paths are likely to occur giving the rate equation (12). The parameters evaluated from

$$k = (k_0[\mathrm{H}^+] + k_1K_1)/([\mathrm{H}^+] + K_1) \quad (12)$$

$$k = (k_1[\mathrm{H}^+] + k_2K_2)/([\mathrm{H}^+] + K_2) \quad (13)$$

$$k = k_1 + k_2K_2[\mathrm{H}^+]^{-1} \quad (14)$$

the experimental data by means of a non-linear least-squares program are $k_0 = (1.07 \pm 0.15) \times 10^3$ dm^3 mol^{-1} s^{-1}, $k_1 = (1.46 \pm 0.1) \times 10^4$ dm^3 mol^{-1} s^{-1}, $K_1 = (6.01 \pm 0.67) \times 10^{-5}$ mol dm^{-3} (pK_1 4.22). In the range pH 6.49–8.0 the relevant rate law is as shown in equation (13). Since pK_2 = 11.10, $K_2 \ll [\mathrm{H}^+]$ under the experimental conditions and equation (13) may be rewritten as equation (14), with $k_1 = (1.63 \pm 0.67) \times 10^4$ dm^3 mol^{-1} s^{-1} and $k_2K_2 = (2.87 \pm 0.2) \times 10^{-3}$ s^{-1}. If K_2 is taken to be 7.94×10^{-12} mol dm^{-3}, $k_2 = (3.61 \pm 0.2) \times 10^8$ dm^3 mol^{-1} s^{-1}. The evaluated parameters (k_0, k_1 and k_2 and K_1, K_2) were used in equation (11) to calculate k values at different pH which showed an excellent agreement to the corresponding experimental values [Fig. 1(*a*)].

Oxidation of Ascorbic Acid by $[\mathrm{Ni^{IV}L^3{}_2}]^{2+}$.—The stoichiometric reaction for the oxidation of ascorbic acid by $[\mathrm{Ni^{IV}L^3{}_2}]^{2+}$ at pH 5.0 can be represented by equation (15). Absorbance

$$[\mathrm{Ni^{IV}L^3{}_2}]^{2+} + \mathrm{H_2A} \longrightarrow [\mathrm{Ni^{II}(HL^3)_2}]^{2+} + \text{dehydroascorbic acid} \quad (15)$$

changes for this reduction are monophasic in the range pH 2.5–8.2, and first-order on both oxidant and reductant. Experiments were carried out with varying concentrations of ascorbic acid with $[\mathrm{H_2A}] = (1.0\text{–}10.0) \times 10^{-4}$ mol dm^{-3} at $[\mathrm{Ni^{IV}L^3{}_2}^{2+}] = 5.0 \times 10^{-5}$ mol dm^{-3} $\{1.0 \times 10^{-5}$ mol dm^{-3} when $[\mathrm{H_2A}] = (1.0\text{–}3.0) \times 10^{-4}$ mol dm$^{-3}\}$, $I = 0.2$ mol dm^{-3}, pH 4.0 and T 30 °C. The evaluated k_{obs} values are listed in Table 1.

The acidity has a pronounced influence on the reaction rate, and is expected to arise from the contribution of proton-associated equilibria of both the oxidant and reductant. At lower pH ($\leqslant 5.0$) a single step two-electron-transfer process occurs whereas at pH $\geqslant 6.0$ the couple is replaced by two separate one-electron-transfer reactions. The initial pH-independent faster step corresponds to $\mathrm{Ni^{IV}} \longrightarrow \mathrm{Ni^{III}}$ conversion [equation (16)] ($E° = 0.634$ V) and the slower pH-dependent

$$[\mathrm{Ni^{IV}L^3{}_2}]^{2+} + \mathrm{e}^- \rightleftharpoons [\mathrm{Ni^{III}L^3{}_2}]^{+} \quad (16)$$

$$[\mathrm{Ni^{III}L^3{}_2}]^{+} + \mathrm{e}^- \rightleftharpoons [\mathrm{Ni^{II}L^3{}_2}] \quad (17)$$

$$[\mathrm{Ni^{III}L^3(HL^3)}]^{2+} + \mathrm{e}^- \rightleftharpoons [\mathrm{Ni^{II}L^3(HL^3)}]^{+} \quad (18)$$

$$[\mathrm{Ni^{III}L^3(HL^3)}]^{2+} \overset{K_\mathrm{h}}{\rightleftharpoons} [\mathrm{Ni^{III}L^3{}_2}]^{+} + \mathrm{H}^+ \quad (19)$$

step to $\mathrm{Ni^{III}} \longrightarrow \mathrm{Ni^{II}}$ conversion [equations (17) ($E° = 0.30$ V) and (18) ($E° = 0.63$ V)] arising from equilibrium (19); the behaviour of the complex upon chemical electron transfer follows the same trend as that found electrochemically.[13]

The oxidation of ascorbic acid by $[\mathrm{Ni^{IV}L^3{}_2}]^{2+}$ yields a bell-shaped curve for a plot of k *vs.* $-\log[\mathrm{H}^+]$ in the range

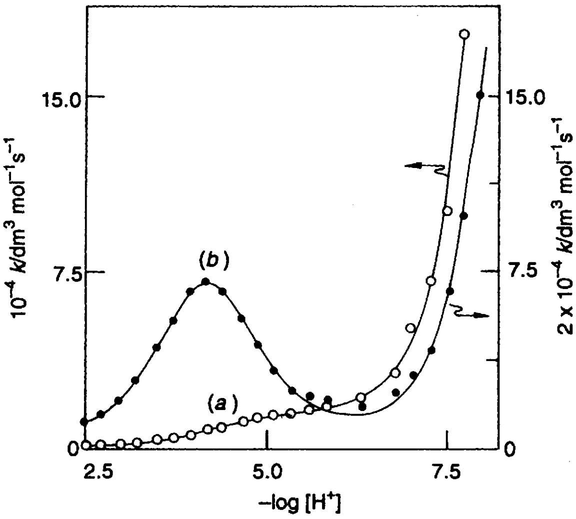

Fig. 1 Variation of k as a function of $-\log[\mathrm{H}^+]$ for the oxidation of ascorbic acid by (*a*) $[\mathrm{Ni^{III}L^1}]^{2+}$ and (*b*) $[\mathrm{Ni^{IV}L^3{}_2}]^{2+}$ at 30 °C with $[\mathrm{NiL}_x{}^{2+}] = 5.0 \times 10^{-5}$ mol dm^{-3}, $I = 0.20$ mol dm^{-3} NaClO$_4$. Calculated values are represented by the solid line, experimental values by points

$-\log[\mathrm{H}^+] = 2.51\text{–}5.36$ [Fig. 1(*b*)]. It is indicative of two protic equilibria—one involving the oxidant and the other ascorbic acid, and also it suggests that one of the deprotonated forms of the reactants has a lower reactivity than that of the protonated form. Oxidation of ascorbic acid by different oxidants[15] and also by $[\mathrm{Ni^{IV}L^2}]^{2+}$ reveals that HA^- is more reactive than $\mathrm{H_2A}$. It appears that the deprotonated form of the nickel complex is less reactive towards a particular reacting species of ascorbic acid. Since $[\mathrm{Ni^{IV}L^3{}_2}]^{2+}$ has a p$K_\mathrm{h} < 1.0$, the protic equilibrium associated with the oxidant is that of $[\mathrm{Ni^{III}L^3{}_2}]^{+}$ [equation (19)] and not $[\mathrm{Ni^{IV}L^3{}_2}]^{2+}$. This is supported by the monophasic reaction traces throughout the experimental pH region (2.51–8.20) even at very low temperature (10 °C) and also by a previous study.[12,13] The absence of the initial faster step may be ascribed to the very fast reaction of $[\mathrm{Ni^{IV}L^3{}_2}]^{2+}$ with ascorbic acid which may be beyond the time-scale (ms) possible with our spectrophotometer.

The reactions (20)–(24) are appropriate under the experimental pH range used. The free radicals thus generated react in a fast step with another nickel(III) species to yield dehydroascorbic acid. The nickel(II) complexes thus generated are protonated and the extent of protonation depends upon the pK values of $[\mathrm{Ni^{II}(HL^3)_2}]^{2+}$ (see above). The general rate law is shown in equation (25), where $k = k_{\mathrm{obs}}/2[\mathrm{H_2A}]_\mathrm{T}$ and 2 is the stoichiometric factor arising from the conversion of $\mathrm{Ni^{III}}$ to $\mathrm{Ni^{II}}$.

$$[\mathrm{Ni^{III}L^3(HL^3)}]^{2+} + \mathrm{H_2A} \xrightarrow{k'_0} [\mathrm{Ni^{II}(HL^3)_2}]^{2+} + \mathrm{HA}^{\bullet} \quad (20)$$

$$[\mathrm{Ni^{III}L^3(HL^3)}]^{2+} + \mathrm{HA}^- \xrightarrow{k'_1} [\mathrm{Ni^{II}(HL^3)_2}]^{2+} + \mathrm{A}^{\bullet-} \quad (21)$$

$$[\mathrm{Ni^{III}L^3{}_2}]^{+} + \mathrm{H_2A} \xrightarrow{k'_2} [\mathrm{Ni^{II}L^3(HL^3)}]^{+} + \mathrm{HA}^{\bullet} \quad (22)$$

$$[\mathrm{Ni^{III}L^3{}_2}]^{+} + \mathrm{HA}^- \xrightarrow{k'_3} [\mathrm{Ni^{II}L^3(HL^3)}]^{+} + \mathrm{A}^{\bullet-} \quad (23)$$

$$[\mathrm{Ni^{III}L^3{}_2}]^{+} + \mathrm{A}^{2-} \xrightarrow{k'_4} [\mathrm{Ni^{II}L^3{}_2}] + \mathrm{A}^{\bullet-} \quad (24)$$

In the range pH 2.51–5.50, reactions (20)–(23) are operative with the rate equation (26). The parameters evaluated by means of a simplex optimization program (with their corresponding

$$k = \frac{k'_0[\mathrm{H}^+]^3 + (k'_1K_1 + k'_2K_\mathrm{h})[\mathrm{H}^+]^2 + k'_3K_1K_\mathrm{h}[\mathrm{H}^+] + k'_4K_1K_2K_\mathrm{h}}{(K_\mathrm{h} + [\mathrm{H}^+])([\mathrm{H}^+]^2 + K_1[\mathrm{H}^+] + K_1K_2)} \tag{25}$$

$$k = \frac{k'_0[\mathrm{H}^+]^2 + (k'_1K_1 + k'_2K_\mathrm{h})[\mathrm{H}^+] + k'_3K_1K_\mathrm{h}}{(K_1 + [\mathrm{H}^+])(K_\mathrm{h} + [\mathrm{H}^+])} \tag{26}$$

standard deviations evaluated by a non-linear least-squares program) are $k'_0 = (2.95 \pm 0.021 \times 10^3)$ dm^3 mol^{-1} s^{-1}, $k'_1 = (9.00 \pm 0.01) \times 10^4$ dm^3 mol^{-1} s^{-1}, $k'_2 = (4.80 \pm 0.01) \times 10^2$ dm^3 mol^{-1} s^{-1}, $k'_3 = (4.53 \pm 0.01) \times 10^3$ dm^3 mol^{-1} s^{-1}, $K_1 = (1.02 \pm 0.01) \times 10^{-4}$ mol dm^{-3} (pK_1 = 3.99) and $K_\mathrm{h} = (4.33 \pm 0.01) \times 10^{-5}$ mol dm^{-3} (pK_h 4.36). Above pH 6.50, there is a steady rate increase with pH consistent with the reactions (23) and (24) following the rate law (27). As the pK_2 value of ascorbic acid is 11.10, $K_2 \ll [\mathrm{H}^+]$

$$k = (k'_3[\mathrm{H}^+] + k'_4K_2)/(K_2 + [\mathrm{H}^+]) \tag{27}$$

$$k = k'_3 + k'_4K_2[\mathrm{H}^+]^{-1} \tag{28}$$

in the chosen pH region (6.5–8.2), equation (27) ultimately reduces to equation (28), with $k'_3 = (5.05 \pm 0.08) \times 10^3$ dm^3 mol^{-1} s^{-1}, $k'_4 = (1.03 \pm 0.03) \times 10^8$ dm^3 mol^{-1} s^{-1} (for $K_2 = 7.94 \times 10^{-12}$ mol dm^{-3}). All the parameters are now included in equation (25) to calculate k at different [H$^+$]. There is an excellent agreement between the experimental and calculated values of k, as depicted in Fig. 1(*b*).

The complexes $[\mathrm{Ni^{IV}L^3}_2]^{2+}$ and $[\mathrm{Ni^{III}L^1}]^{2+}$ have pseudo-octahedral NiN$_6$ geometry with moderate reduction potential values and stability in aqueous solution.[6–10] No estimates of the ligand-exchange rate of the nickel-(IV) and -(III) complexes are available but it is expected to be slow (< 10^2 s^{-1}).[17] The low ligand-substitution labilities of nickel-(IV) and -(III) complexes with HL^3, H$_2$L^2 and HL^1 are likely to favour an outer-sphere electron-transfer mechanism. In fact, nickel-(IV) and -(III) complexes generally react by an outer sphere mechanism,[13,19–25] although there are a few exceptions where an inner-sphere process is likely to occur.[17,26] In the present investigation, there was no spectral evidence to support an inner-sphere process.

To justify an outer-sphere pathway an attempt was made to apply the Marcus theory for evaluating the theoretical electron-transfer rate constants (k_{12}) by using equations (29)–(33),[27]

$$\log K_{12} = n\Delta E°/0.06023 \text{ at } 30\,°\mathrm{C} \tag{29}$$

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{\frac{1}{2}} \cdot W_{12} \tag{30}$$

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4[\ln (k_{11}k_{22})/Z^2 + (w_{11} + w_{22})/RT]} \tag{31}$$

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

$$w_{ij} = 4.23 \times Z_iZ_j/[a(1 + 0.328a\sqrt{I})] \tag{33}$$

where k_{11} is the self-exchange rate constant for the oxidising complexes, k_{22} are those for the couples H$_2$A$^{\bullet+}$–H$_2$A, HA$^\bullet$–HA$^-$ and A$^{\bullet-}$–A^{2-} and K_{12} is the equilibrium constant for the electron-transfer reaction. It is necessary to include the work terms w_{ij} and factor f_{12} in the present calculations owing to the wide range of driving forces and charge types involved. The data are listed in Table 2. The term Z in equation (31) is the collision frequency for which a value of 1.0 × 10^{11} dm^3 mol^{-1} s^{-1} has been used. Z_i and Z_j are the ionic charges on the reactants, R is the universal gas constant [1.98 × 10^{-3} kcal mol^{-1} (≈8.28 × 10^{-3} kJ mol^{-1})], a is the centre to centre distance (Å) when the reacting species are in contact. The radii of nickel-(IV) and -(II) complexes are evaluated from the equation $4/3\pi r^3 = M/N\rho$, where M is the molecular weight of the corresponding complexes, N the Avogadro number and ρ represents the densities of $[\mathrm{Ni^{IV}L}_x]^{2+}$ and $[\mathrm{Ni^{II}(H_2L)}_x]^{2+}$ complexes. We used reported densities[25,26] which gave radii of 5.16, 5.10, 5.08 and 5.02 Å for $[\mathrm{Ni^{II}(H_2L^2)}]^{2+}$, $[\mathrm{Ni^{IV}L^2}]^{2+}$, $[\mathrm{Ni^{II}(HL^3)_2}]^{2+}$ and $[\mathrm{Ni^{IV}L^3}_2]^{2+}$ respectively.[31,32] The radii of Ni$^{\mathrm{III}}$–L^2 and Ni$^{\mathrm{III}}$–L^3 were taken as the average of the Ni$^{\mathrm{IV}}$–L$_x$ and Ni$^{\mathrm{II}}$–L$_x$ radii, and found to be 5.13 and 5.05 Å for the Ni$^{\mathrm{III}}$–L^2 and Ni$^{\mathrm{III}}$–L^3 complexes respectively.

However, we have used a constant value of 5.1 Å for all the Ni–L complexes for our calculations;[33] the radius of ascorbic acid is reported to be 3.5 Å.[28] Self-exchange rate constants (k_{22}/dm^3 mol^{-1} s^{-1}) and standard reduction potentials ($E°$/V) of the different couples of ascorbic acid[12,34] are 10^9, 10^7 and 10^6, and 1.35, 0.93 and 0.019 for H$_2$A$^{\bullet+}$–H$_2$A, HA$^\bullet$–HA$^-$ and A$^{\bullet-}$–A^{2-} respectively. Using these parameters we have calculated the cross-electron-transfer rate constants for the oxidation of H$_2$A, HA$^-$ and A^{2-} by nickel complexes and also for other reported reactions, which are listed in Table 2. An inspection of these data reveals that the experimental rate constants for the oxidation of H$_2$A and HA$^-$ by all the nickel(III) complexes are at least ≈2–7 orders of magnitude higher than the corresponding calculated values. This indirectly supports an inner-sphere process. On the contrary, the experimental and calculated electron-transfer rate constants for the oxidation of A^{2-} by these nickel(III) complexes are in excellent agreement, and support the operation of an outer-sphere route, as has been shown for other reported outer-sphere reactions (Table 2). The large difference in the experimental and calculated electron-transfer rate constants for the oxidation of H$_2$A and HA$^-$ indicate a drastic change in mechanism from an outer- to an inner-sphere process. The higher reactivity of the protonated nickel(III) species compared to the corresponding deprotonated ones is accompanied by hydrogen-bonding effects with the protonated reducing agents (H$_2$A or HA$^-$), since the reduction to nickel(II) requires additional protonation on the complex. This could be achieved by the exchange of a hydrogen atom from the protonated reducing species, say from HA$^-$, leading not only to $[\mathrm{Ni(H_2L^2)}]^{2+}$, $[\mathrm{Ni(HL^3)_2}]^{2+}$ or $[\mathrm{Ni^{II}(HL^1)}]^{2+}$ but also to the dehydroascorbate product. Thus for the oxidation of H$_2$A and HA$^-$, the reaction is expected to proceed through the formation of a hydrogen-bonded species between the hydrogen atom of H$_2$A or HA$^-$ and the oximato oxygen of the ligand. This could provide a low-energy pathway and the internal electron transfer[35] can be represented by Scheme 1 for the oxidation of HA$^-$ by $[\mathrm{Ni^{III}L}_x]^+$ as a representative one. In the $[\mathrm{Ni^{III}L}_x]^+$ oxidant the nickel(III) is the electron-acceptor and the oximato oxygen the proton-acceptor site. Scheme 1 ensures the formation of the protonated nickel(II) complex as the product. The dilemma posed by changes in the degree of protonation accompanying electron transfer is not encountered in A^{2-} which can simply be accommodated by an outer-sphere route. The proton-coupled electron transfer is not apparent from kinetic results. However the electrochemical studies on the complex system do support the concerted nature of the electron-transfer process. The situation is comparable to the atom-transfer mechanism proposed by Binstead and Meyer[36] in the reaction between ruthenium(IV) and ruthenium(II) complexes. Our rationale is supported by the excellent agreement between the experimental and calculated rate constants obtained by the application of Marcus theory for the oxidation of A^{2-} by $[\mathrm{Ni^{III}L^3}_2]^+$ and $[\mathrm{Ni^{III}L^1}]^{2+}$ complexes.

$$\begin{tikzcd}
{[\mathrm{Ni^{III}L}_x]^+ + \mathrm{HA}^-} \arrow[r, shift left, "K"] & \{[\mathrm{Ni^{III}L}_x]^+ \cdots \mathrm{HA}^-\} \arrow[l, shift left] \arrow[r, "k"] & \{\mathrm{Ni^{II}(HL}_x)\mathrm{A}\} \arrow[d, "\text{fast}"] \\
 & & {[\mathrm{Ni^{II}(HL}_x)]^+ + \mathrm{A}^{\bullet-}}
\end{tikzcd}$$

Scheme 1

Table 2 Cross-reaction kinetic data[a]

				k_{12exp}/dm^3 mol^{-1} s^{-1}			k_{12calc}/dm^3 mol^{-1} s^{-1}		
Oxidant	$E°$/V	r/Å	k_{11}/dm^3 mol^{-1} s^{-1}	H_2A	HA^-	A^{2-}	H_2A	HA^-	A^{2-}
$[Ni^{III}L^2]^{+}$ [b]	0.42	5.10	2.0×10^3	—	1.36×10^4	—	—	1.59 (39.4)	—
$[Ni^{III}(HL^2)]^{2+}$ [b]	0.64	5.10	1.0×10^3	—	3.02×10^5	—	—	4.51×10^2 (4.74×10^3)	—
$[Ni^{III}L^3{}_2]^{+}$ [c]	0.30	5.10	8.0×10^3	4.80×10^3	4.79×10^3	1.03×10^8	3.62×10^{-7}	0.11 (4.61)	2.85×10^8
$[Ni^{III}L^3(HL^3)]^{2+}$ [c]	0.63	5.10	5.0×10^2	2.95×10^3	9.0×10^4	—	1.23×10^{-2}	2.2×10^2 (2.74×10^3)	—
$[Ni^{III}L^1]^{2+}$ [c,d]	0.49	5.10	6.0×10^2	1.07×10^3	1.55×10^4 (av.)	3.37×10^8 3.61×10^8	1.52×10^{-4}	8.10 (1.58×10^2)	3.20×10^8
$[Ru(NH_3)_4(bipy)]^{3+}$ [e]	0.53	4.40	2.20×10^6	—	2.10×10^5	—	—	1.80×10^3 (5.82×10^4)	—
$[IrCl_6]^{2-}$ [f]	0.892	4.40	2.30×10^5	*ca.* 4.0×10^2	2.80×10^7	—	4.87×10^2	1.05×10^6 (5.78×10^6)	—
$[Fe(CN)_5\{(H_2N)_2CS\}]^{2-}$ [e]	0.35	5.0	1.0×10^5	—	66.0	8.80×10^7	—	1.01 (50.1)	8.32×10^7
$[Fe(phen)_3]^{3+}$ [e,f]	1.09[g]	6.80[g]	5.0×10^8	*ca.* 3.0×10^4 [e]	1.50×10^9 [d]	—	10.4×10^5	1.80×10^9 (4.92×10^9)	—
$[CoW_{12}O_{40}]^{5-}$ [e,f]	1.00	5.0	1.70	7.74×10^1 [e]	2.40×10^5 [d]	—	4.99×10^2	1.07×10^5 (4.66×10^5)	—
$[Fe(bipy)_3]^{3+}$ [f]	1.06[g]	6.80[g]	5.0×10^8 [g]	—	5.40×10^8	—	—	$1.25 \times 10^9)$ (3.41×10^9)	—
$[IrBr_6]^{2-}$ [f]	0.84[g]	6.80	2.0×10^8 [g]	2.0×10^2	5.90×10^7	—	69.26	8.06×10^6 (5.29×10^7)	—
$[Co(terpy)_2]^{3+}$ [e]	0.27	6.60	1.72×10^2	—	—	8.50×10^6	—	—	18.6×10^6
$[Ru(NH_3)_5(py)]^{3+}$ [e]	0.32	3.80	1.10×10^5	—	—	6.0×10^9	—	—	16.4×10^9
$[Ru(dipic)_2]^{-}$ [e]	0.27	5.20	1.0×10^7	—	—	2.30×10^8	—	—	2.37×10^8
$Hcat^{-}$ [e]	0.04	3.30	1.60×10^6	—	—	1.30×10^6	—	—	1.90×10^6

[a] Evaluation of the rate constants using Marcus cross relation involves the following parameters for ascorbic acid: k_{22}/dm^3 mol^{-1} s^{-1} = 10^9 ($H_2A^{\bullet +}$–H_2A), 10^7 ($HA^{\bullet}$–HA^-), 10^6 ($A^{\bullet -}$–A^{2-}) and $E°$/V = 1.35 ($H_2A^{\bullet +}$–H_2A), 0.93($HA^{\bullet}$–HA^-), 0.019 ($A^{\bullet -}$–A^{2-}) (ref. 12) and the radius of all the species of ascorbic acid = 3.5 Å (ref. 15). The parenthetical $k_{12}(HA^-)$ values were calculated using $E°$ = 0.71 V and k_{22} = 1.0×10^5 dm^3 mol^{-1} s^{-1} (ref. 30). bipy = Bipyridine, phen = 1,10-phenanthroline, py = pyridine, terpy = 2,2′: 6′,2″-terpyridine and dipic = pyridine-2,6-dicarboxylic acid, H_2cat = catechol. [b] Ref. 12, 30 °C. [c] Refs. 6 and 17, 30 °C. [d] Ref. 11, 30 °C. [e] Ref. 28, 25 °C. [f] Ref. 28, 20 °C. [g] Ref. 29.

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References

1 R. A. Marusak, C. Sharp and A. G. Lappin, *Inorg. Chem.*, 1990, **29**, 4453.

2 A. Chakravorty, *Coord. Chem. Rev.*, 1974, **13**, 1.

3 R. S. Drago and E. I. Baucom, *Inorg. Chem.*, 1972, **11**, 2064.

4 E. I. Baucom and R. S. Drago, *J. Am. Chem. Soc.*, 1971, **93**, 6469.

5 G. Sproul and G. D. Stucky, *Inorg. Chem.*, 1973, **12**, 2898.

6 A. Chakravorty, *Isr. J. Chem.*, 1985, **25**, 99.

7 K. Nag and A. Chakravorty, *Coord. Chem. Rev.*, 1980, **33**, 87.

8 J. G. Mahanty, R. P. Singh and A. Chakravorty, *Inorg. Chem.*, 1975, **14**, 2178.

9 A. N. Singh, R. P. Singh, J. G. Mahanty and A. Chakravorty, *Inorg. Chem.*, 1977, **16**, 2597.

10 J. G. Mahanty, R. P. Singh, A. N. Singh and A. Chakravorty, *J. Indian Chem. Soc.*, 1977, **54**, 219.

11 A. N. Singh and A. Chakravorty, *Inorg. Chem.*, 1980, **19**, 969.

12 A. G. Lappin, M. C. M. Larangeira and L. Youde-Owei, *J. Chem. Soc., Dalton Trans.*, 1981, 721.

13 A. G. Lappin and M. C. M. Laranjeira, *J. Chem. Soc., Dalton Trans.*, 1982, 1861.

14 M. Ali, S. K. Saha and P. Banerjee, *J. Chem. Soc., Dalton Trans.*, 1990, 187.

15 S. Gangopadhyay, S. K. Saha, M. Ali and P. Banerjee, *Int. J. Chem. Kinet.*, 1991, **23**, 105; M. Kimura and M. Yamamoto, *J. Chem. Soc., Dalton Trans.*, 1982, 423

16 J. H. Roe, *Methods of Biochemical Analysis*, Interscience, New York, 1954, vol. 1, pp. 115–139.

17 A. McAuley, C. J. Macdonald, L. Spencer and P. R. West, *J. Chem. Soc., Dalton Trans.*, 1988, 2279.

18 D. H. Macartney and A. McAuley, *Can. J. Chem.*, 1981, **59**, 135.

19 D. H. Macartney and A. McAuley, *Inorg. Chem.*, 1983, **22**, 2062.

20 A. G. Lappin, M. C. M. Laranjeira and R. D. Peacock, *Inorg. Chem.*, 1983, **22**, 786.

21 A. G. Lappin, D. P. Martone and P. Osvath, *Inorg. Chem.*, 1985, **24**, 4187.

22 A. G. Lappin, D. P. Martone, P. Osvath and R. A. Marusak, *Inorg. Chem.*, 1988, **27**, 1863.

23 D. H. Macartney and A. McAuley, *J. Chem. Soc., Dalton Trans.*, 1984, 103.

24 A. E. Allan, A. G. Lappin and M. C. M. Laranjeira, *Inorg. Chem.*, 1984, **23**, 477.

25 D. H. Macartney and D. W. Thompson, *Inorg. Chem.*, 1989, **28**, 2195.

26 S. F. Munn, A. M. Lannon, M. C. M. Laranjeira and A. G. Lappin, *J. Chem. Soc., Dalton Trans.*, 1984, 1371.

27 *Inorganic Reactions and Methods*; ed. J. J. Zuckerman, VCH, Deerfield Beach, FL, 1986, vol. 15, pp. 13–47.

28 E. Pelizzetti, E. Mentasti and E. Pramanro, *Inorg. Chem.*, 1978, **17**, 1181.

29 R. Sarala and D. M. Stanbury, *Inorg. Chem.*, 1990, **29**, 3456.

30 D. H. Macartney and N. Sutin, *Inorg. Chim. Acta*, 1983, **74**, 221; A. McAuley, L. Spencer and P. R. West, *Can. J. Chem.*, 1985, **63**, 1198; S. Steenken and P. Neta, *J. Phys. Chem.*, 1979, **83**, 1134.

31 J. Korvenranta, H. Saarinen and M. Nasakkala, *Inorg. Chem.*, 1982, **21**, 4296.

32 H. Saarinen, J. Korventanta and M. Nasakkala, *Acta Chem. Scand., Ser. A*, 1980, **34**, 443.

33 S. Bhattacharya, M. Ali, S. Gangopadhyay and P. Banerjee, *J. Chem. Soc., Dalton Trans.*, 1994, 3733.

34 N. H. Williams and J. K. Yandell, *Aust. J. Chem.*, 1982, **35**, 1133 and refs. therein.

35 A. McAuley and M. A. Olatunji, *Can. J. Chem.*, 1977, **55**, 3335.

36 R. A. Binstead and T. J. Meyer, *J. Am. Chem. Soc.*, 1987, **109**, 3287.

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