Studies in Nickel(IV) Chemistry. Part 4.† Kinetics of the Electron Transfer from L-Ascorbic Acid to Tris(dimethylglyoximato)nickelate(IV) in Aqueous Medium ‡

Sridhara Acharya, Gautam Neogi, and Rama Krushna Panda *
Department of Chemistry, Berhampur University, Berhampur 760 007, Orissa, India
Dorai Ramaswamy
Chemical Laboratories, Central Leather Research Institute, Madras 600 020, India

The kinetics of electron transfer from L-ascorbic acid (H_2A) to tris(dimethylglyoximato)nickelate(IV), $[Ni(dmg)_3]^{2-}$, follow a pseudo-first-order disappearance of the Ni^{IV} complex in aqueous medium at 35 °C and I = 0.25 mol dm^{-3}. The pseudo-first-order rate constant ($k_{obs.}$) conforms to $k_{obs.} = k_{ad} + k_{red}$, where k_{ad} refers to the pseudo-first-order rate constant for the independently determined proton-assisted decomposition of the Ni^{IV} complex and k_{red} to that for the intermolecular reduction of Ni^{IV} by H_2A. The rate constants for the proton-assisted decomposition range from 4.6 to 2.6 × 10^{-7} s^{-1} (pH range 1.6—12.3) and those for the reduction reaction range from 5.1 × 10^2 to 8 dm^3 mol^{-1} s^{-1} (pH range 1.6—11.1). The results are interpreted in terms of a probable mechanism involving a rate-determining outer-sphere one-electron transfer from the reductant to the oxidant Ni^{IV} species present in the solution, followed by a subsequent and kinetically indistinguishable rapid reaction of the Ni^{III} intermediate.

The biochemical significance of the oxidation of L-ascorbic acid has stimulated numerous studies of mechanisms of electron transfer in metal complexes. The majority of studies so far have been confined to the elucidation of the mechanism of electron transfer between ascorbic acid and one-electron oxidants.[1-11] While significant inferences can be drawn from such studies, there remains a paucity of information pertaining to the mechanism in the presence of two-electron oxidants. Even though a few recent investigations describing the oxidation of ascorbic acid by two-electron oxidants have appeared,[2b,9,12-15] no generalised mechanistic interpretations have been arrived at. A very recent study [16] and a related study [17a] on the details of the kinetics of oxidation of ascorbic acid by a nickel(IV) complex in the pH region 1—6 have been reported. Tris(dimethylglyoximato)nickelate(IV), $[Ni(dmg)_3]^{2-}$ (dmg^{2-} = dimethylglyoximate dianion), in which the unusual and higher oxidation state of +4 of the metal is highly stabilised due to the σ- and π-donor character of the ligand environment, is found to be an effective two-electron oxidant.[18,19] The present report attempts to describe the probable mechanistic pathways involved in the electron transfer from L-ascorbic acid to the Ni^{IV} complex.

Experimental

Materials.—All solutions were made up using freshly prepared doubly-distilled water (distilled from an all-glass apparatus containing *ca.* 1 × 10^{-4} mol dm^{-3} ethylenediaminetetra-acetate). L-Ascorbic acid (H_2A) was an AnalaR grade (B.D.H.) sample and was used without further purification; its concentration in solution was estimated by a recent analytical procedure.[20] Aqueous solutions of H_2A were freshly prepared before use; they were standardised, appropriately diluted and their pH adjusted, as required, when employed for runs. The preparation and characterization of $K_2[Ni(dmg)_3]$ and its aqueous solutions were as described earlier.[18,19] Other reagents used were of reagent grade. Standard buffer solutions for maintaining the pH were prepared in water using potassium salts. The pH values were measured both before and after the reactions and were found to be reproducible. Corrections due to ionic strength effects [21] were applied in calculating $[H^+]$ from the pH. Throughout the work, the pH values listed refer to the corrected mean pH (± 0.01 units). Potassium chloride was used as the supporting electrolyte to maintain the ionic strength (I).

Kinetics.—Reactions were monitored for the disappearance of the Ni^{IV} complex at 460 nm (ε_{460} = 9 600 dm^3 mol^{-1} cm^{-1}) as described earlier.[19] In a typical experiment, a freshly prepared aqueous solution of the Ni^{IV} complex was rapidly mixed with an equal volume of the reductant solution at the desired pH, I, and temperature (± 0.1 °C), and the progress of the reaction monitored continuously as a function of time. Pseudo-first-order rate constants were calculated making use of the usual expression and were found to remain practically constant for more than three half-lives of the Ni^{IV} disappearance in the range 440—480 nm or when the reactions (in representative runs) were conducted in a nitrogen atmosphere. The pseudo-first-order disappearance of the Ni^{IV} complex was also found to be satisfied in the range $6 \times 10^{-6} \leqslant [Ni^{IV}]_0 \leqslant 1.5 \times 10^{-4}$ mol dm^{-3} where $[Ni^{IV}]_0$ is the initial concentration of $[Ni(dmg)_3]^{2-}$. The rate constants in replicates (two to seven) were reproducible to ±5%. The spontaneous oxidation of ascorbic acid was found to be negligible under the conditions employed.[2a]

Stoicheiometry and Products.—Stoicheiometric experiments were conducted under a nitrogen atmosphere at pH 9.2 and 6.8 with $[Ni^{IV}]_0 > [H_2A]_0$. In five determinations at each pH and employing $[Ni^{IV}]_0$ = 0.8 × 10^{-4}—1.6 × 10^{-4} and $[H_2A]_0$ = 0.1 × 10^{-4}—0.6 × 10^{-4} mol dm^{-3}, the unreacted Ni^{IV} was measured spectrophotometrically at the end of each reaction. One mol of ascorbate was found to have reacted with 1.02 ± 0.03 mol of the Ni^{IV} complex [equation (i)]. The stoicheiometric runs could not be conducted at lower pH values since the proton-assisted decomposition of the Ni^{IV} complex interfered with the measurements.

$$HA^- + [Ni(dmg)_3]^{2-} + 3\,H_2O \longrightarrow A' + [Ni(Hdmg)_2] + H_2dmg + 3\,OH^- \quad (i)$$

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† Part 3, G. Neogi, S. Acharya, R. K. Panda, and D. Ramaswamy, *J. Chem. Soc., Dalton Trans.*, 1983, 1239.

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Table 1. Pseudo-first-order rate constants for the reduction of $[Ni(dmg)_3]^{2-}$ by ascorbic acid in aqueous medium; $I = 0.25$ mol dm^{-3}, 35 °C, $[Ni^{IV}]_0 = 2.5 \times 10^{-5}$—$5 \times 10^{-5}$ mol dm^{-3}

pH [a]	$10^3[H_2A]_0$/ mol dm^{-3}	$10^3k_{obs.}$/s^{-1}	10^3k_{ad}/s^{-1} [b]	10^3k_{red}/s^{-1} [c]
5.05 [d]	3.6	163 ± 5	1.9	161
	7.5	326 ± 13		324
	10	450 ± 15		448
	10	453 ± 11		451 [e]
	10	440 ± 18		438 [f]
6.34 [g]	1.2	14.3 ± 0.4	0.1	14.2
	3.6	42 ± 1		42
	5.2	60 ± 2		60
	9.4	110 ± 3		110
	12	140 ± 5		140
	15	180 ± 5		180
	20	230 ± 9		230
	20	240 ± 7		240 [e]
	20	220 ± 9		220 [f]
7.6 [g]	1.2	12.1 ± 0.4	0.015	12.1
	3.6	36 ± 1		36
	9.4	93 ± 3		93
	20	198 ± 6		198
	20	192 ± 8		192 [e]
	20	190 ± 7		190 [f]
8.4 [h]	1.2	11.9 ± 0.3	0.0125	11.9
	3.6	36 ± 1		36
	5.2	52 ± 2		52
	9.5	94 ± 3		94
	15	149 ± 4		149
	15	152 ± 5		152 [e]
	15	140 ± 5		140 [f]
	15	146 ± 6		146 [i]
	25	240 ± 7		240
9.2 [h]	1.2	12.5 ± 0.3	0.0115	12.5
	3.0	32 ± 1		32
	3.1	32.2 ± 0.9		32.2 [j]
	3.5	35 ± 1		35 [k]
	3.5	35 ± 1		35
	3.8	37 ± 1		37
	3.9	39 ± 1		39
	5.2	51 ± 2		51 [k]
	6.1	62 ± 2		62
	6.5	67 ± 2		67
	6.7	65 ± 2		65
	7.0	66 ± 2		66
	7.4	73 ± 2		73
	7.4	73 ± 2		73 [i]
	7.4	72 ± 2		72 [e]
	7.6	76 ± 2		76
	9.2	92 ± 3		92
	9.4	90 ± 3		90
	12	110 ± 3		110
	14	122 ± 4		122
	25	233 ± 7		233
10.1 [h]	1.2	11.5 ± 0.3	0.0095	11.5
	3.6	34 ± 1		34
	5.2	49 ± 1		49
	9.5	88 ± 3		88
	15	140 ± 4		140
	20	187 ± 5		187
	25	230 ± 7		230
	25	238 ± 9		238 [e]
	25	221 ± 9		221 [f]
	25	224 ± 8		224 [i]

Table 1 (*continued*)

[a] Corrected pH (±0.01 units). [b] Calculated using equation (iii) from independent data of ref. 19. [c] $k_{red} = k_{obs.} - k_{ad}$ at pH 5.05 and 6.34; and $k_{red} \approx k_{obs.}$ at pH 7.6, 8.4, 9.2, and 10.1. [d] Potassium hydrogen phthalate–KOH buffer. Use of potassium acetate–acetic acid buffer did not alter the rate. [e] Under an atmosphere of nitrogen gas. [f] In the presence of 5×10^{-5} mol dm^{-3} added $Na_2(H_2edta)$. [g] $H_2PO_4^-$–OH^- buffer. [h] BO_3^{3-}–H^+/OH^- buffer. [i] In the presence of 1×10^{-4} mol dm^{-3} added acrylonitrile (N_2 atmosphere). [j] 10^3k_{red} = 10.6, 16.8, and 50.9 s^{-1} at 26, 30, and 40 °C, respectively. [k] At pH 8.8; k_{red} is independent of pH in the range 8.8—9.2. Use of tris(hydroxymethyl)aminomethane-HCl buffer at pH 8.8 did not alter the rate.

The $[Ni(Hdmg)_2]$ was estimated microgravimetrically and dimethylglyoxime was identified qualitatively.[19] Dehydroascorbic acid (A′) was identified by Roe's method [22] to be the product of the oxidation of ascorbic acid, as in many earlier studies.[2] A reaction mixture of the Ni^{IV} complex (2.5×10^{-2} mol dm^{-3}, 5 cm^3) and HA^- (1.5×10^{-2} mol dm^{-3}, 5 cm^3) at pH 9.2 after completion of the reaction (evidenced by the constancy in the absorbance of the unreacted Ni^{IV}) was filtered and the precipitate of $[Ni(Hdmg)_2]$ collected. A dilute solution of nickel(II) sulphate (0.1 mol dm^{-3}, 2 cm^3) was added to the filtrate, the solution mixture was shaken well, and again filtered. The filtrate (1 cm^3) was acidified with sulphuric acid (pH *ca.* 1) and added to a reagent mixture (5 cm^3) containing 2,4-dinitrophenylhydrazine and excess of thiourea in a 25 cm^3 volumetric flask. The flask was left aside at *ca.* 50 °C for 4 h and the resulting solution cooled in an ice-bath. The intensity of the red solutions was measured spectrophotometrically (after dilution to obtain a solution of measurable absorbance) at 525 nm and the concentration of dehydroascorbic acid calculated with reference to a calibration curve.

Proton-dissociation Constants.—The first and second proton-dissociation constants (K_{a1} and K_{a2}) of H_2A were determined by pH titrations in an atmosphere of nitrogen gas using a Systronics 335 digital pH meter equipped with glass and saturated calomel electrodes. The average values of K_{a1} and K_{a2} were found respectively to be 1.26×10^{-4} and 8.47×10^{-12} mol dm^{-3} at 35 °C and $I = 0.25$ mol dm^{-3} (KCl), in agreement with earlier reported values.[2,4]

Results

In order to examine possible pathways for electron transfer from ascorbic acid to the Ni^{IV} complex, a series of experiments was performed maintaining pseudo-first-order excess of $[H_2A]_0$ over $[Ni^{IV}]_0$. Since the Ni^{IV} complex underwent proton-assisted decomposition [19] (with accompanying intramolecular electron transfer) in the pH range employed, the measured pseudo-first-order rate constant ($k_{obs.}$) would conform to equation (ii), where k_{ad} refers to the pseudo-first-order rate constant for proton-assisted decomposition of the Ni^{IV} complex and is a function of $[H^+]$, and k_{red} to that for the reduction reaction and is a function of $[H^+]$ and $[H_2A]_0$.

$$k_{obs.} = k_{ad} + k_{red} \qquad \text{(ii)}$$

At pH $\gtrsim$ 7, k_{ad} was found to be negligible in comparison to k_{red} so that $k_{obs.} \approx k_{red}$. In the pH range 7.6—10.1, k_{red} was found to be almost linearly dependent on the initial analytical concentration of ascorbic acid, $[H_2A]_0$; linear dependence of k_{red} ($= k_{obs.} - k_{ad}$) on $[H_2A]_0$ was also observed at pH 5.05 and 6.34 in the range of $[H_2A]_0$ studied (Table 1).

The reduction rates were found to be almost insensitive to the presence of added $Na_2(H_2edta)$ (H_4edta = ethylenediaminetetra-acetic acid) (Table 1), implying that the reaction is not subject to extensive trace metal-ion catalysis under the conditions employed. The lack of significant influence of a radical-trapping agent on the kinetics was seen from the lack of effect of acrylonitrile on the rate or the lack of any detectable polymerization (in a nitrogen atmosphere).

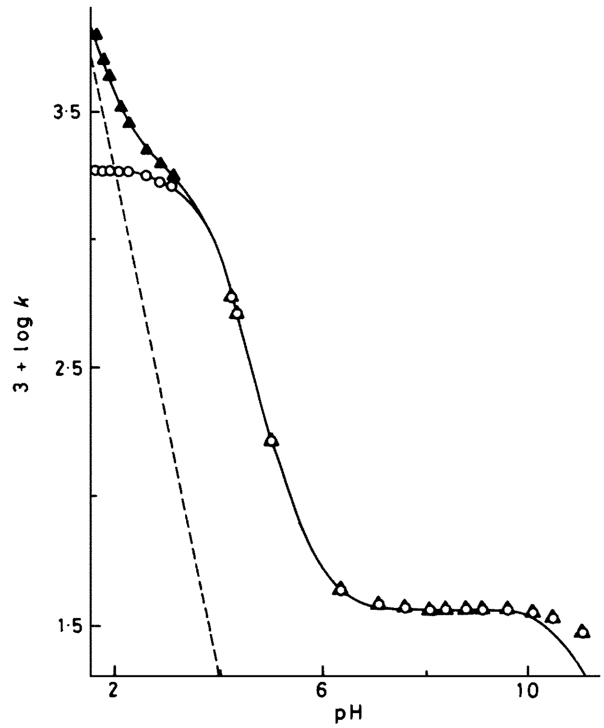
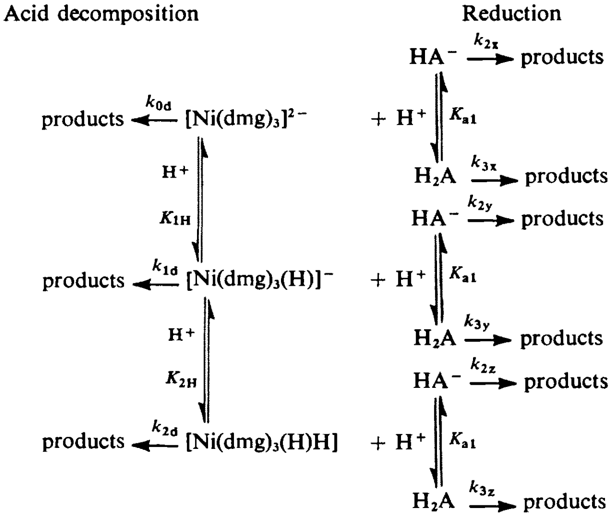


Figure 1. Plots of log k *vs.* pH; $k_{obs.}$ denoted by ▲ and k_{red} by ○. The dotted line is drawn from values of k_{ad}

The pH dependence of the rate constants was studied in the pH range 1.6—11.1 using appropriate buffers. If the values of k_{ad} at the respective pH values [calculated from the independent data [19] of the proton-assisted decomposition using equation (iii)] were subtracted from $k_{obs.}$, values of k_{red} were obtained (Table 2). Figure 1 presents the plots of the logarithm of rate constant ($k_{obs.}$, k_{red}, and k_{ad}) against the pH of the medium and clearly indicates that k_{red} contains terms of different orders in $[H^+]$. The value of k_{red} was found to remain consistently higher than k_{ad} in the pH range 2.25—11.1, the difference between them being more prominent in the higher pH region; however, at pH $\lesssim$ 2.25, k_{ad} still increased with decreasing pH and was higher than k_{red}, while saturation in k_{red} was attained (at pH $\lesssim$ 2.25).

Scheme 1 outlined below is consistent with the kinetic behaviour of the reduction reaction and envisages probable interactions of the acid ascorbate anion (HA^-) and ascorbic acid (H_2A) species with the unprotonated $\{[Ni(dmg)_3]^{2-}\}$ and protonated forms $\{[Ni(dmg)_3(H)]^-$ and $[Ni(dmg)_3(H)H]\}$ of the Ni^{IV} complex leading to outer-sphere electron transfer(s) from the reductant species to the oxidant complex species.

The rate law derivable from Scheme 1 is given by equation (ii), where k_{ad} and k_{red} are defined by equations (iii) and (iv). Equation (iv) can be rearranged to give equation (iva).



Scheme 1. The reactivity of A^{2-} is assumed to be negligible

The pH dependence of k_{ad} (from independent experiments) was explained [19] in terms of equation (iii), where K_{1H} and K_{2H} respectively refer to the potentiometrically determined values of the first and second protonation constants of the Ni^{IV} complex, and k_{0d}, k_{1d}, and k_{2d} to the solvent-assisted, first-protonation-assisted, and second-protonation-assisted decomposition rate constants.

A least-squares analysis of the Z and $[H^+]$ data, in accordance with equations (iv) and (iva), resulted in the values of $k_{2x}K_{a1}$, $(k_{3x} + k_{2y}K_{1H}K_{a1})$, $(k_{3y}K_{1H} + k_{2z}K_{1H}K_{2H}K_{a1})$, and $(k_{3z}K_{1H}K_{2H})$ as $(3.9 \pm 0.1) \times 10^{-4}$ s^{-1}, $(8.9 \pm 0.2) \times 10^{7}$ dm^3 mol^{-1} s^{-1}, $(3.69 \pm 0.02) \times 10^{13}$ dm^6 mol^{-2} s^{-1}, and $(1.61 \pm 0.04) \times 10^{14}$ dm^9 mol^{-3} s^{-1} respectively. The k_{red} (calc.) values, estimated from equation (iv) employing the above values, were found to agree excellently with experimentally determined k_{red} (Table 2). Unambiguous values of k_{2x} and k_{3z} could be calculated from these resolved constants as 3.1 ± 0.1 dm^3 mol^{-1} s^{-1} and $(5.1 \pm 0.1) \times 10^2$ dm^3 mol^{-1} s^{-1} respectively. The individual reactivities of k_{3x} and k_{2y}, and k_{3y} and k_{2z}, occurring as mixed terms in equation (iv), cannot easily be separated. However, in limiting cases, if it is assumed that (*a*) $k_{3x} \gg k_{2y}K_{1H}K_{a1}$, then $k_{3x} \approx 8.9 \times 10^7$ dm^3 mol^{-1} s^{-1} or (*b*) if $k_{3x} \ll k_{2y}K_{1H}K_{a1}$, then $k_{2y} \approx 9.9$ dm^3 mol^{-1} s^{-1}. Similarly, in other limiting cases, either $k_{3y} \approx 5.2 \times 10^2$ dm^3 mol^{-1} s^{-1} or $k_{2z} \approx 9.3 \times 10^5$ dm^3 mol^{-1} s^{-1}. Average values of the various constants are listed in Table 3. The k_{3x} step for the $[Ni(dmg)_3]^{2-}$–H_2A reaction, for which the ambiguous value calculated is very high, is most probably not operative since the species $[Ni(dmg)_3]^{2-}$ is almost non-existent in the pH region where H_2A is prevalent; in that event, the k_{2y} step may be more important and $k_{2x} \approx k_{2y} \approx$ *ca.* 10 dm^3 mol^{-1} s^{-1}. Either or both of the steps represented by k_{3y} and k_{2z} (for which ambiguous values have been obtained) may be important, but the individual reactivities in the mixed term are not as easily determined. If k_{3y} is more important, then $k_{3y} \approx k_{3z}$. On the other hand, if k_{2z} is more so, then $k_{2z} \gg k_{3z}$.

$$k_{ad} = \frac{k_{0d} + k_{1d}K_{1H}[H^+] + k_{2d}K_{1H}K_{2H}[H^+]^2}{1 + K_{1H}[H^+] + K_{1H}K_{2H}[H^+]^2} \qquad \text{(iii)}$$

$$k_{red} = \frac{[H_2A]_0\{k_{2x}K_{a1} + (k_{3x} + k_{2y}K_{1H}K_{a1})[H^+] + (k_{3y}K_{1H} + k_{2z}K_{1H}K_{2H}K_{a1})[H^+]^2 + k_{3z}K_{1H}K_{2H}[H^+]^3\}}{(1 + K_{1H}[H^+] + K_{1H}K_{2H}[H^+]^2)(K_{a1} + [H^+])} \qquad \text{(iv)}$$

$$k_{red}\,(1 + K_{1H}[H^+] + K_{1H}K_{2H}[H^+]^2)(K_{a1} + [H^+])/[H_2A]_0 = Z = \{k_{2x}K_{a1} + (k_{3x} + k_{2y}K_{1H}K_{a1})[H^+] + (k_{3y}K_{1H} + k_{2z}K_{1H}K_{2H}K_{a1})[H^+]^2 + k_{3z}K_{1H}K_{2H}[H^+]^3\} \qquad \text{(iva)}$$

Table 2. Pseudo-first-order rate constants for the reduction of $[Ni(dmg)_3]^{2-}$ by ascorbic acid in aqueous medium; I = 0.25 mol dm^{-3}, 35 °C, $[Ni^{IV}]_0 = (2.5—5) \times 10^{-5}$ mol dm^{-3}, $[H_2A]_0 = (3.5—3.7) \times 10^{-3}$ mol dm^{-3}

pH [a]	$10^3k_{obs.}$/s^{-1}	10^3k_{ad}/s^{-1} [b]	10^3k_{red}/s^{-1} [c]	10^3 k_{red}(calc.)/s^{-1} [d]
1.6	6 400 ± 190	4 600	1 800	1 800
1.75	5 100 ± 150	3 300	1 800	1 800
1.84 [e]	4 500 ± 140	2 700	1 800	1 800
2.1	3 400 ± 100	1 600	1 800	1 800
2.25	2 900 ± 90	1 100	1 800	1 800
2.6	2 300 ± 70	500	1 800	1 800
2.85	2 000 ± 60	280	1 700	1 700
3.1	1 800 ± 50	160	1 640	1 600
4.26	600 ± 20	10.9	589	600
4.35	520 ± 16	8.8	511	520
5.03	163 ± 5	2.0	161	160
6.34	42 ± 1	0.1	42	42
7.1	37 ± 1	0.02	37	37
7.6	36 ± 1	0.015	36	36
8.1	36 ± 1	*f*	36	36
8.4	36 ± 1	*f*	36	36
8.8	36 ± 0.9	*f*	36	36
9.1	35 ± 0.8	*f*	35	35
9.2	35 ± 1	*f*	35	35
9.6	35 ± 0.9	*f*	35	34
10.1	34 ± 1	*f*	34	32
10.5	32 ± 1	*f*	32	28
11.1	28 ± 1	*f*	28	20

[a] Corrected pH (±0.01 units). Key to buffers: buffer (pH range); HCl–KCl (1.59—2.1), hydrogenphthalate–HCl (2.25—3.1), acetate–acetic acid (4.26—5.03), $H_2PO_4^-$–OH^- (6.34—7.6), BO_3^{3-}–H^+/OH^- (8.1—10.5), HPO_4^{2-}–OH^- (11.1). [b] k_{ad} at the corresponding pH is calculated from the independent data (ref. 19) using equation (iii). [c] $k_{red} \doteq k_{obs.} - k_{ad}$ (pH 1.6—6.34) and $k_{red} = k_{obs.}$ (pH $\gtrsim$ 7). [d] Calculated from a least-squares fit of data to equation (iv). [e] Cl_3CCO_2H–KCl buffer. [f] $k_{ad} \ll k_{obs.}$.

Table 3. Average values of the various constants in the reduction of $[Ni(dmg)_3]^{2-}$ by ascorbic acid in aqueous medium (I = 0.25 mol dm^{-3}, 35 °C)

Constant	Average value	Ref.
K_{1H}/dm^3 mol^{-1}	7.08×10^{10}	19
K_{2H}/dm^3 mol^{-1}	4.46	19
k_{0d}/s^{-1}	2.6×10^{-7}	19
k_{1d}/s^{-1}	1.16×10^{-5}	19
k_{2d}/s^{-1}	44.3	19
K_{a1}/mol dm^{-3}	1.26×10^{-4}	This work
k_{2x}/dm^3 mol^{-1} s^{-1}	3.1 [a]	This work
k_{3x} [b]/dm^3 mol^{-1} s^{-1}	~8.9×10^7 [c]	This work
k_{2y} [b]/dm^3 mol^{-1} s^{-1}	~9.9 [a]	This work
k_{3y} [d]/dm^3 mol^{-1} s^{-1}	~5.2×10^2	This work
k_{2z} [d]/dm^3 mol^{-1} s^{-1}	~9.3×10^5 [a]	This work
k_{3z}/dm^3 mol^{-1} s^{-1}	5.1×10^2 [a]	This work

[a] Proposed pathways. [b] k_{3x} and k_{2y} are kinetically indistinguishable pathways. [c] Value unlikely. [d] k_{3y} and k_{2z} are kinetically indistinguishable pathways.

Discussion

In spite of the apparent complexity of the rate law [equation (iv)], reasonably simple assumptions can be made and inferences on the reactivity pattern drawn. If the steps represented by k_{2x}, k_{2y}, k_{2z}, and k_{3z} are important, then $k_{2x} \approx k_{2y}$, $k_{2z} \gg k_{2y}$, and $k_{2z} \gg k_{3z}$. In that event the reactivities appear to follow the structural indifference of the unprotonated and the monoprotonated Ni^{IV} species,[19] the electrostatic charge on the diprotonated and the monoprotonated Ni^{IV} species, and the redox potentials of HA^- and H_2A, respectively (see later).

$$[Ni^{IV}(dmg)_3(H)]^- + HA^- \xrightarrow{k_5} [Ni^{III}(dmg)_3(H)]^{2-} + HA^{\bullet} \quad (v)$$

$$[Ni^{III}(dmg)_3(H)]^{2-} + HA^{\bullet} \xrightarrow{k_6} [Ni^{II}(Hdmg)_2] + dmg^{2-} + A' \quad (vi)$$

Scheme 2. $k_6 \gg k_5$

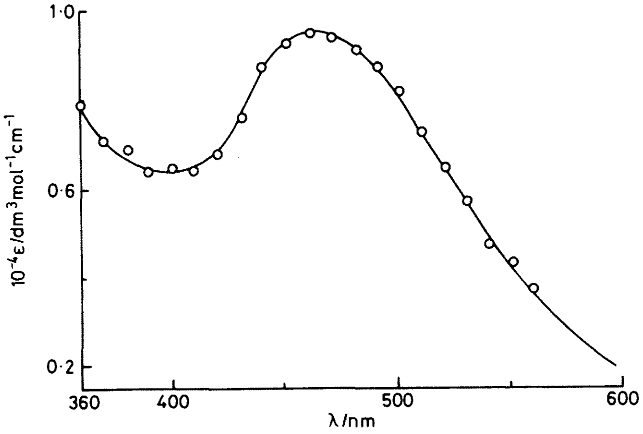


Figure 2. Representative spectra of the nickel(IV) complex (———) (1×10^{-4} mol dm^{-3}) and a reaction mixture (○) containing $[Ni^{IV}]_0 = 1 \times 10^{-4}$ and $[H_2A]_0 = 3 \times 10^{-3}$ mol dm^{-3} (aqueous medium, I = 0.25 mol dm^{-3}, 35 °C, pH 9.2, time-scale on 50-ms mode)

Ascorbic acid has been found in many systems to give an intermediate oxidation product of an ascorbate radical. However, the present kinetic data together with the failure to observe an effect of a radical-trapping agent on the rate are insufficient to regard its presence in appreciable concentrations. Ascorbate radical, when formed, would disappear *via* a rapid reaction with the intermediate Ni^{III} complex or a disproportionation [6] much faster than the initiation of acrylonitrile polymerization.

Ascorbic acid, in its redox reactions with various oxidants, exhibits a dichotomous behaviour of either proceeding by substitution-controlled routes or by outer-sphere pathways. The exact requirements which necessitate the operation of either of the mechanisms are, however, not well identified. Even though in a number of studies, the formation of metal ion–ascorbic acid precursor (or successor) intermediates, prior to the actual electron transfer, has been well documented from spectroscopic and kinetic evidence, in numerous other instances the inner-sphere mechanism has been envisaged merely by speculation, sometimes on the basis of insufficient kinetic results. Studies in which information has been obtained regarding the intermediates include, for example, those on oxidants like Cu^{2+} (in the presence of molecular O_2),[2a,23a] Cu^{II} complexes,[23b] VO^{2+},[24a] VO_2^+,[1a,2b] 'vanadyl tetrasulphophthalocyanine' (+O_2),[24b] U^{VI},[2c] and Nb^V.[25]

We believe that the rate-determining step of the present reaction most probably involves outer-sphere one-electron transfer from the reductant to the oxidant Ni^{IV} species (*cf.* Scheme 2 for a representative sequence), the subsequent and kinetically inconsequential step being the rapid decay of the paramagnetic Ni^{III} intermediate, on the basis of the following arguments (*a*)—(*g*).

(*a*) No limiting kinetics of the rate on $[H_2A]_0$ were observed in the range of $[H_2A]_0$ employed.

(*b*) Point-by-point spectra of the reaction mixture on the stopped-flow assembly at pH 4.6, 6.2, or 9.2 were not different ($\lambda_{max.}$ or ε) from those of the Ni^{IV} complex at the corresponding pH. Representative spectra of the original Ni^{IV} complex and the reaction mixture at pH 9.2 are presented in Figure 2. (The Aminco stopped-flow assembly has a nominal mixing time of 2 ms. The point-by-point absorbance values were recorded at wavelength intervals of 10 nm using the time-scale on 50-ms mode. Under the conditions, there was no appreciable decomposition of the Ni^{IV} complex.) *No* abrupt initial absorbance change at 460 nm could be observed as soon as the reactants were mixed.

(*c*) The fact that $[Ni(dmg)_3]^{2-}$ is substitution-inert (as the solvent-assisted decomposition rate constant, k_{0d}, is 2.6×10^{-7} s^{-1} at 35 °C)[19] and that the second-order rate constant for the interaction of $[Ni(dmg)_3]^{2-}$ and HA^- is very much greater than the solvent-assisted decomposition rate constant (*i.e.*, $k_{2x} \gg k_{0d}$) give definite evidence, even at first glance, for the operation of the outer-sphere reaction of these species. The reduction rates of the first-protonated Ni^{IV} species are also higher than the decomposition rates (*i.e.*, $k_{2y} \gg k_{1d}$), suggesting outer-sphere routes.

(*d*) The reactivity orders mentioned earlier also suggest the operation of outer-sphere electron transfer. Data on the proton-assisted decomposition of the nickel(IV) complex have suggested[19] that the first (outside) protonation of the complex occurs at a dioximate oxygen forming an intramolecular hydrogen-bonding network between dioximate oxygens of two ligands and that during this process there is little change in the original pseudo-octahedral structure; the rate-determining decomposition step of the monoprotonated species proceeds by simultaneous intramolecular oxidation of a ligand unit and dissociation. It has also been shown that the diprotonated species is a ' kinetic intermediate ' and the second protonation occurs most probably *via* a direct proton addition to a (ring-opened) nitrogen site (caused by the first protonation). Thus in the pH range studied, there are three important oxidant species: $[Ni(dmg)_3]^{2-}$, $[Ni(dmg)_3(H)]^-$, and $[Ni(dmg)_3(H)H]$, of which the first two are structurally similar and the third (which incidentally is the most electrophilic of the three) is different from the other two. These predict the reactivity orders: $k_{2x} \approx k_{2y}$ and $k_{2z} \gg k_{2x} \approx k_{2y}$ (rather than $k_{3z} \approx k_{3y}$ in the other limiting case mentioned earlier). The reactivity order, $k_{2z} \gg k_{3z}$, is compatible with outer-sphere electron transfer, for $(\log k_{2z} - \log k_{3z})/\Delta E^{\ominus} \approx 8$ as predicted on the basis of redox potential considerations.[4,26] ($\Delta E^{\ominus}$ refers to the difference in the redox potentials for the couples $E^{\ominus}_{HA\cdot/HA^-} = 0.93$ V and $E^{\ominus}_{H_2A\cdot^+/H_2A} = 1.33$ V).[26] The fact that the magnitude of k_{red} is independent of that of k_{ad} in the pH range studied also supports the idea of outer-sphere electron transfer.

(*e*) The rate-determining step of Scheme 2 should be accompanied by a very high activation enthalpy * as the reaction involves the formation of two reactive species.[27] Therefore, it should be possible to obtain evidence for the intermediacy of the Ni^{III} species at low temperatures. Indeed, evidence for the paramagnetic Ni^{III} intermediate has been obtained by e.s.r. experiments. For example, the formation of Ni^{III} was indicated by an e.s.r. signal at $g_{av} \sim 2.12$ when solutions of the Ni^{IV} complex (1×10^{-4} mol dm^{-3}) and ascorbic acid (1×10^{-4} to 3×10^{-4} mol dm^{-3}) were mixed at 0—2 °C (pH 9.2 or 3), the mixture was immediately quenched in liquid nitrogen and the spectrum recorded.[18]

(*f*) The redox potentials for the various oxidant/reduced forms of the complexes derived from $[Ni(dmg)_3]^{2-}$ are not known,† but generally values for the Ni^{IV}–Ni^{III} couples are smaller than for the Ni^{III}–Ni^{II} couples for analogous systems.[16,17,28,29] One-electron transfer rates involving the Ni^{IV} complex are, in general, comparatively smaller[16,17] than those involving Ni^{III} (*i.e.*, $k_5 \ll k_6$ in Scheme 2).

There is no information about the lability of these Ni^{III} complexes although the axial positions of tetragonal Ni^{III} complexes are relatively labile, and the substitution rates[30] generally of the order of *ca.* 10^2 s^{-1}. The k_{2y} value of *ca.* 10 dm^3 mol^{-1} s^{-1}, if assumed to correspond to the reaction of the protonated Ni^{III} species, $[Ni(dmg)_3(H)]^{2-}$, with HA^-, is smaller than the general substitution rates of Ni^{III} complexes. As a matter of fact, all the resolved second-order rate constants (except perhaps k_{2z}) are smaller than the Ni^{III} substitution rates. This implies that inner-sphere electron transfer would have been expected if the reaction were to involve the the Ni^{III} complex as a kinetically important species, and this is in contradiction to the present experimental observations.

(*g*) Evidence from e.s.r. on the paramagnetic Ni^{III} intermediate discounts the possibility of a single-step two-electron transfer process in this redox system.

During the course of the present investigation, Lappin *et al.*[16,17a] reported the reaction taking place between HA^- and $[Ni^{IV}L]^{2+}$ (L = 3,14-dimethyl-4,7,10,13-tetra-azahexadeca-3,13-diene-2,15-dione dioximate dianion). Initially a scheme, similar to Scheme 2, was preferred,[16] but later the kinetic data were reinterpreted, on the basis of e.s.r. and visible spectroscopic data for the protonated Ni^{III} species, in terms of a scheme which envisaged rapid formation of the Ni^{III} species $[NiL]^+$ and $[Ni(HL)]^{2+}$, followed by the rate-limiting outer-sphere one-electron transfer from the reductant HA^- to these Ni^{III} oxidant species.[17a] There was a single rapid absorbance change at 500 nm, much faster than the rate of reduction observed. In the present redox reaction (the half-lives of which are much larger than those of the reaction involving $[NiL]^{2+}$ and HA^-) no rapid initial absorbance change could be detected on the stopped-flow time-scale, thus precluding the possibility of such a situation. Incidentally, the acid-dependent and acid-independent outer-sphere second-order rate constants for the reactions of HA^- with $[Ni^{III}L]^+$ and $[Ni^{III}(HL)]^{2+}$ were 1.36×10^4 and 3.02×10^5 dm^3 mol^{-1} s^{-1} at 25 °C and $I = 0.1$ mol dm^{-3} ($NaClO_4$) in aqueous medium.[16,17a] No comparison of the present data can, however, be made with those obtained by Lappin *et al.*[16,17a] since the reaction steps, the oxidation potentials of the complexes, and the net electrostatic charge on the complexes in the two systems are widely different.

In conclusion, the intermolecular reduction reaction most probably proceeds by rate-determining outer-sphere one-electron transfer(s) from the ascorbic acid to the oxidant Ni^{IV} species, the subsequent rapid and kinetically indistinguishable step(s) being the reaction of the Ni^{III} intermediate.

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* The apparent activation parameters could not be isolated from the values of the net activation parameters (*e.g.*, $\Delta H^{\ddagger} = 85$ kJ mol^{-1}, $\Delta S^{\ddagger} = 2$ J K^{-1} mol^{-1}, range 26 — 40 °C, pH 9.2) because the reaction involves multi-step processes of protonation, acid decomposition, and reduction.

† The pH-dependent redox potentials of the couples of the various nickel species derived from $[Ni(dmg)_3]^{2-}$ could not be determined from cyclic voltammetric experiments because the voltammograms gave irreproducible results due to the decomposition of the complexes.

References

1 (*a*) K. Kustin and D. L. Toppen, *Inorg. Chem.*, 1973, **12**, 1404; (*b*) R. R. Grinstead, *J. Am. Chem. Soc.*, 1960, **82**, 3464; (*c*) S. P. Mushran, M. C. Agrawal, R. M. Mehrotra, and R. Sanehi, *J. Chem. Soc., Dalton Trans.*, 1974, 1460; (*d*) U. S. Mehrotra, M. C. Agrawal, and S. P. Mushran, *J. Inorg. Nucl. Chem.*, 1970, **32**, 2325; (*e*) U. S. Mehrotra, M. C. Agrawal, and S. P. Mushran, *J. Phys. Chem.*, 1969, **73**, 1996.

2 (*a*) M. M. T. Khan and A. E. Martell, *J. Am. Chem. Soc.*, 1967, **89**, 1587, 4176, 7104; (*b*) *ibid.*, 1968, **90**, 3386, 6011; (*c*) *ibid.*, 1969, **91**, 4668, and refs. therein.

3 R. A. Rickman, R. L. Sorensen, K. O. Watkins, and G. Davies, *Inorg. Chem.*, 1977, **16**, 1570,

4 E. Pelizzetti, E. Mentasti, and E. Pramauro, *Inorg. Chem.*, 1976, **15**, 2898; 1978, **17**, 1181; *J. Chem. Soc., Dalton Trans.*, 1978, 61 and refs. therein.

5 F. L. Harris and D. L. Toppen, *Inorg. Chem.*, 1978, **17**, 74.

6 B. H. J. Bielski, H. W. Ritcher, and P. C. Chaw, *Ann. N.Y. Acad. Sci.*, 1975, **256**, 231; B. H. J. Bielski, A. O. Allen, and H. A. Schwarz, *J. Am. Chem. Soc.*, 1981, **103**, 3516; C. Greenwood and G. Palmer, *J. Biol. Chem.*, 1965, **240**, 3660.

7 K. Bhatt and K. C. Nand, *Z. Phys. Chem. (Leipzig)*, 1979, **260**, 834.

8 K. C. Rajanna, Y. R. Rao, and P. K. Saiprakash, *Indian J. Chem., Sect. A*, 1979, **17**, 66.

9 U. S. Mehrotra and S. P. Mushran, *Can. J. Chem.*, 1970, **48**, 1148; R. Senehi, R. M. Mehrotra, and S. P. Mushran, *J. Inorg. Nucl. Chem.*, 1975, **37**, 1753; S. P. Mushran and M. C. Agrawal, *J. Sci. Ind. Res.*, 1977, **36**, 274.

10 K. Hayakawa, S. Minami, and S. O. Nakamura, *Bull. Chem. Soc., Jpn.*, 1973, **46**, 2783.

11 L. Pekkarinen and H. Lemmetyinen, *Suom. Kemistil. B*, 1972, **45**, 144; E. V. Shtamm and Yu. Skurlatov, *Zh. Fiz. Khim.*, 1974, **48**, 1454; Yu. Skurlatov, *Int. J. Chem. Kinet.*, 1980, **12**, 347.

12 V. I. Spitsyn, K. I. Popov, V. F. Churaev, T. A. Karpulhina, G. K. Mailieve, and V. L. Zafirova, *Zh. Neorg. Khim.*, 1980, **25**, 163.

13 W. Weiss, *Ann. N.Y. Acad. Sci.*, 1975, **258**, 190.

14 M. K. Joshi and S. Raoot, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 2331; S. Raoot and V. G. Vaidya, *Indian J. Chem., Sect. A*, 1978, **16**, 996.

15 E. A. Maksimyuk and I. O. N. Kh. S. Platiny, *Izv. Akad. Nauk SSSR*, 1955, 180.

16 A. G. Lappin, M. C. M. Laranjeira, and L. Y.-Owei, *J. Chem. Soc., Dalton Trans.*, 1981, 721.

17 (*a*) A. G. Lappin and M. C. M. Laranjeira, *J. Chem. Soc., Dalton Trans.*, 1982, 1861; (*b*) A. G. Lappin, M. C. M. Laranjeira, and R. D. Peacock, *Inorg. Chem.*, 1983, **22**, 786.

18 R. K. Panda, S. Acharya, G. Neogi, and D. Ramaswamy, *J. Chem. Soc., Dalton Trans.*, 1983, 1225.

19 G. Neogi, S. Acharya, R. K. Panda, and D. Ramaswamy, *J. Chem. Soc., Dalton Trans.*, 1983, 1233.

20 P. V. Ramana, K. Mohan Rao, and N. Venkateswar Rao, *J. Indian Chem. Soc.*, 1980, **57**, 235.

21 'Handbook of Analytical Chemistry,' ed. L. Meites, McGraw Hill, New York, 1963, sect. 1, p. 8.

22 J. H. Roe, 'Methods of Biochemical Analysis,' Interscience, New York, vol. 1, pp. 115—139.

23 (*a*) D. M. Wagnerova, E. Schwertnerova, and J. Veprek-Siska, *Collect. Czech. Chem. Commun.*, 1976, **41**, 2473 and refs. therein; (*b*) R. J. Jameson and N. J. Blackburn, *J. Inorg. Nucl. Chem.*, 1975, **37**, 809.

24 (*a*) E. F. Kries, *Russ. J. Inorg. Chem.*, 1978, **23**, 1004 and refs. therein; (*b*) D. M. Wagnerova, J. Blanck, G. Smettan, and J. Veprek-Siska, *Collect. Czech. Chem. Commun.*, 1978, **43**, 2105 and refs. therein.

25 R. N. Gupta and B. K. Sen, *J. Inorg. Nucl. Chem.*, 1975, **37**, 1548.

26 D. H. Macartney and A. McAuley, *Can. J. Chem.*, 1981, **59**, 132 and refs. therein.

27 D. R. Stranks, in 'Modern Coordination Chemistry—Principles and Methods,' eds. J. Lewis and R. G. Wilkins, Interscience, New York, 1960, ch. 2, p. 103.

28 K. Nag and A. Chakravorty, *Coord. Chem. Rev.*, 1980, **33**, 87 and refs. therein.

29 D. H. Macartney and A. McAuley, *Can. J. Chem.*, 1983, **61**, 103.

30 R. I. Haines and A. McAuley, *Inorg. Chem.*, 1980, **19**, 719.

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