DALTON

Kinetics of oxidation of ascorbate by tetranuclear cobalt(III) complexes ('hexols') in aqueous solution

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The kinetics of oxidation of L-ascorbic acid (H_2A) by cobalt(III) hexols, $[Co\{CoL_4(\mu\text{-}OH)_2\}_3]^{6+}$ [$L_4 = (NH_3)_4$, $(en)_2$, or tren; en = ethane-1,2-diamine, tren = tris(2-aminoethyl)amine], was studied as a function of pH, L-ascorbic acid concentration, temperature and ionic strength, using stopped-flow and conventional spectrophotometric techniques. The rate of the reaction is first order with respect to the concentration of each reactant and increases as $[H^+]$ decreases. The kinetic data indicate involvement of the monoprotonated and deprotonated ascorbate species (HA^- and A^{2-}) in the redox process. For $L_4 = (NH_3)_4$ the rate constants, k_2 and k_3 are 0.22 ± 0.02 and $(5.51 \pm 0.09) \times 10^5$ dm^3 mol^{-1} s^{-1} respectively at 25 °C, and the corresponding activation parameters are $\Delta H^{\ddagger}_2 = 103 \pm 7$ kJ mol^{-1}, $\Delta S^{\ddagger}_2 = 89 \pm 22$ J K^{-1} mol^{-1} and $\Delta H^{\ddagger}_3 = 46 \pm 3$ kJ mol^{-1} and $\Delta S^{\ddagger}_3 = 19 \pm 11$ J K^{-1} mol^{-1}. The variations in rate constants and activation parameters for the series of complexes mentioned above are discussed. The Fuoss theory was applied to the redox process to estimate the ion-pair formation constant and the rate constant for the electron transfer.

Much interest has been centred around electron-transfer reactions involving cobalt(III) complexes with L-ascorbic acid.[1-7] These studies seek to elucidate the mechanistic details of the redox processes in order to acquire information concerning the kinetic and thermodynamic parameters, such as the self-exchange rate coefficients, activation parameters, redox potentials and reorientation activation functions, as well as intermediates and products of the reactions. More recently, a lot of attention has been devoted to the study of polynuclear transition-metal complexes. We have been particularly interested in the study of mixed-metal and mixed-valence compounds as well as compounds with metal centres in various chemical environments.[8 10] Such complexes include the well known tetranuclear cobalt(III) hexols $[Co\{CoL_4(OH)_2\}_3]^{6+}$ (L = amine) which have cobalt(III) moieties in two chemically distinguishable environments. Our studies include the oxidation of L-ascorbic acid by a series of these complexes. From the structure of the complexes, two rate-determining pathways are possible. The central cobalt(III) of a hexol complex, being in a $Co^{III}O_6$ site, is expected to be more readily reduced than the outer cobalt(III) moieties which are in $Co^{III}N_4O_2$ sites.[11] However, the outer cobalt(III) groups are more accessible to reaction with the ascorbate species.

This work is concerned with determining which of the two mechanisms is involved in the rate-determining step of the reduction of the cobalt(III) hexols by L-ascorbic acid.

Experimental

Materials

All chemicals were either Reagent or Analar grade. Distilled water was obtained from a Corning all-glass distillation unit. Deionised water was obtained by passing distilled water through a Milli-Q reagent-grade water system (Millipore Corporation, Bedford, MA) and was used to make up solutions for all physical measurements. Nitrogen was obtained from Jamaica Oxygen and Acetylene Limited. Stock lithium ascorbate solution (0.25 mol dm^{-3}) was prepared as reported previously.[1]

Preparation of complexes

The complexes were prepared by previously reported methods.[12-14] The purity of the complexes were determined by UV/VIS spectrophotometry and elemental analysis (Butterworth Laboratories Ltd.).

$[Co\{Co(NH_3)_4(OH)_2\}][ClO_4]_6\cdot 6H_2O$: $\varepsilon_{504} = 212$ and $\varepsilon_{627} = 126$ dm^3 mol^{-1} cm^{-1} (lit.,[12] $\varepsilon_{504} = 212$ and $\varepsilon_{627} = 126$ dm^3 mol^{-1} cm^{-1}). Found: H, 3.75; Cl, 17.25; Co, 18.15; N, 13.00. Calc.: H, 4.40; Cl, 17.10; Co, 18.70; N, 13.50%).

$[Co\{Co(en)_2(OH)_2\}][NO_3]_6\cdot 3H_2O$ (en = ethane-1,2-diamine): $\varepsilon_{492} = 361$ and $\varepsilon_{620} = 109$ dm^3 mol^{-1} cm^{-1} (lit.,[15] $\varepsilon_{492} = 363$ and $\varepsilon_{620} = 110$ dm^3 mol^{-1} cm^{-1}) (Found: C, 12.45; H, 5.25; Co, 18.15; N, 21.60. Calc.: C, 12.40; H, 5.55; Co, 20.30; N, 21.75%). $[Co\{Co(tren)(OH)_2\}_3][ClO_4]_6\cdot 8H_2O$ [tren = tris(2-aminoethyl)amine]: $\varepsilon_{495} = 302$ and $\varepsilon_{622} = 110$ dm^3 mol^{-1} cm^{-1} (lit.,[14] $\varepsilon_{495} = 310$ and $\varepsilon_{622} = 117$ dm^3 mol^{-1} cm^{-1} (Found: C, 14.35; H, 4.70; Cl, 14.05; Co, 14.90; N, 10.75. Calc.: C, 14.25; H, 5.05; Cl, 14.00; Co, 15.55; N, 11.10%).

Kinetic measurements

The reactions were studied under pseudo-first-order conditions as a function of the decrease in absorbance with time at λ_{max} 627, 620 and 622 nm for the NH_3, en and tren complexes respectively. These wavelengths indicate changes for the hexol complexes only, without complications from the reactions involving the ensuing cobalt(III) mononuclear intermediates, $[CoL(H_2O)_2]^{3+}$, which have λ_{max} at 504, 492 and 502 nm for the NH_3, en and tren species respectively. An ionic strength of 0.5 mol dm^{-3} was maintained using standard lithium perchlorate solution, the pH range was 3.7–5.7 (acetate buffer), the temperature range 20–40 °C, the total ascorbate concentration $[A]_T$ 0.01–0.05 mol dm^{-3} and the initial complex concentration 5×10^{-4} mol dm^{-3}. The faster reactions were studied using a Hi-Tech Scientific model SF-51 stopped-flow unit connected to a SU-40 UV/VIS spectrophotometer. Constant temperature was maintained with a Haake GH constant-temperature water-bath fitted with a Haake D8 circulating pump.

The slower reactions were studied by conventional spectrophotometry using a Philips Scientific PU8800 UV/VIS

Table 1 Pseudo-first-order rate constants as a function of $[A]_T$ for the reaction of L-ascorbic acid with cobalt(III) hexols at pH 5.65 ± 0.02; 25.1 °C; initial [complex] = 5×10^{-4} mol dm^{-3} and I = 0.5 mol dm^{-3} ($LiClO_4$)

$[Co\{Co(NH_3)_4(OH)_2\}_3]^{6+}$		$[Co\{Co(en)_2(OH)_2\}_3]^{6+}$		$[Co\{Co(tren)(OH)_2\}_3]^{6+}$	
10^2 $[A]_T$ mol dm^{-3}	10^2 k_{obs}/ s^{-1}	10^2 $[A]_T$ mol dm^{-3}	10^2 k_{obs}/ s^{-1}	10^2 $[A]_T$ mol dm^{-3}	10^2 k_{obs}/ s^{-1}
1.0	2.10	1.0	1.74	1.0	0.95
1.5	3.22	1.5	2.58	1.5	1.35
2.0	4.12	2.0	3.44	2.0	1.74
2.5	5.26	2.5	4.25	2.5	2.12
3.0	6.37	3.0	5.07	3.0	2.68
3.5	7.40	3.5	6.09	3.5	3.06
4.0	9.13	4.0	6.92	4.0	3.42
4.5	9.80	4.5	7.70	4.5	3.76
5.0	10.41	5.0	8.85	5.0	4.11

Table 2 Pseudo-first order rate constants as a function of temperature and pH for the reaction of L-ascorbic acid with $[Co\{Co(NH_3)_4(OH)_2\}_3]^{6+}$ at $[A]_T = 2.5 \times 10^{-2}$ mol dm^{-3}; initial [complex] = 5×10^{-4} mol dm^{-3} and I = 0.5 mol dm^{-3} ($LiClO_4$)

20.1 °C		25.1 °C*		30.2 °C		35.0 °C		40.1 °C	
pH	10^2 k_{obs}/s^{-1}	pH	10^2 k_{obs}/s^{-1}	pH	10^2 k_{obs}/s^{-1}	pH	10^2 k_{obs}/s^{-1}	pH	10^2 k_{obs}/s^{-1}
4.49	0.30	4.05	0.41	4.49	1.36	4.47	2.54	4.46	4.87
4.67	0.45	4.28	0.59	4.67	1.87	4.66	3.45	4.64	7.06
4.91	0.74	4.50	0.75	4.92	2.89	4.90	5.38	4.89	10.46
5.20	1.16	4.67	1.08	5.20	4.43	5.18	8.62	5.18	16.15
5.42	1.68	4.91	1.70	5.42	6.82	5.40	12.87	5.39	24.31
5.67	2.58	5.20	2.57	5.67	10.51	5.66	19.11	5.66	37.37
		5.44	4.21						
		5.65	6.37						

* $[A]_T = 3.0 \times 10^{-2}$ mol dm^{-3}.

spectrophotometer or a Hewlett-Packard HP8452A diode-array spectrophotometer connected to a Fisher Scientific constant-temperature circulator. Pseudo-first-order rate constants for the slower reactions were determined using a STATGRAPHICS computer program[16] in the non-linear mode. The error in each reported k_{obs} value is less than 3%.

All pH measurements were made using an Orion Research Expandable Ion Analyser (model EA920) digital pH meter, fitted with a Cole-Parmer combination electrode. The pH meter was calibrated using standard buffer solutions. The pH readings were converted into $[H^+]$ by using the appropriate activity coefficient of H^+ at the particular temperature and ionic strength.[17]

Results and Discussion

Nature of the reactions

Mixing equal volumes of equimolar solutions of the hexol complexes and ascorbic acid at pH ⩾ 6 resulted in an instantaneous change from the brown of the hexol solution to pink. The spectrum of the resulting solution is identical to that of the corresponding mononuclear diaqua complex at the particular pH. At pH ⩽ 4 it corresponds to that of a mixture of the hexol and the diaqua complex. Adding the resulting mixtures to a solution of ammonium thiocyanate in acetone confirms the presence of cobalt(II).

Stoichiometry

Stoichiometric studies included the use of spectrophotometric titrations and analysing for cobalt(II) using a previously reported method.[18] In a typical spectrophotometric titration, aliquots of the ascorbic acid solution were added to solutions of the hexol complex. The absorbance at selected wavelengths was then plotted *versus* ascorbate concentration.

The above observations and stoichiometric results indicate that at pH 4.5 L-ascorbic acid reacts in a 1:1 ratio with the complexes, forming 3 mol of $[CoL(H_2O)_2]^{3+}$ and 1 mol of cobalt(II) per mol hexol. The diaqua species then reacts with ascorbic acid to give cobalt(II). The kinetics of the latter reactions was previously reported.[1] At pH 8 L-ascorbic acid reacts in a 1:2 ratio with the hexol complexes.

Mechanism

Based on the qualitative and stoichiometric studies it is evident that the tetranuclear cobalt(III) hexols are reduced to cobalt(II), producing *cis*-diaquacobalt(III) species as intermediates. The variation of k_{obs} with $[A]_T$ is shown in Table 1 for the three complexes, those with temperature and pH in Tables 2, 3 and 4 for the NH_3, en and tren complexes respectively. It has been confirmed that the hydroxo bridges of the hexol complexes do not undergo protonation.[12] In addition, the acid hydrolysis of these complexes is very slow even in strong acids, hence the $[H^+]$ dependence observed can only be attributed to the speciation of L-ascorbic acid. Thus, the mechanism illustrated by equations (1)–(8) can be proposed.

$$H_2A \overset{K_{a1}}{\rightleftharpoons} HA^- + H^+ \quad (1)$$

$$HA^- \overset{K_{a2}}{\rightleftharpoons} A^{2-} + H^+ \quad (2)$$

$$[Co^{III}{}_4] + H_2A \xrightarrow{k_1} 3Co^{III} + Co^{II} + H_2A^{\bullet +} \quad (3)$$

$$[Co^{III}{}_4] + HA \xrightarrow{k_2} 3Co^{III} + Co^{II} + HA^{\bullet} \quad (4)$$

$$[Co^{III}{}_4] + A^{2-} \xrightarrow{k_3} 3Co^{III} + Co^{II} + A^{\bullet -} \quad (5)$$

Table 3 Pseudo-first-order rate constants as a function of temperature and pH for the reaction of L-ascorbic acid with $[\mathrm{Co}\{\mathrm{Co(en)_2(OH)_2}\}_3]^{6+}$ (conditions as in Table 2)

20.1 °C		25.1 °C*		30.2 °C		35.0 °C		40.1 °C	
pH	$10^2\,k_{obs}/s^{-1}$	pH	$10^2\,k_{obs}/s^{-1}$	pH	$10^2\,k_{obs}/s^{-1}$	pH	$10^2\,k_{obs}/S^{-1}$	pH	$10^2\,k_{obs}/s^{-1}$
4.48	0.49	4.02	0.43	4.47	1.58	4.47	2.85	4.46	4.83
4.68	0.60	4.25	0.68	4.67	1.98	4.66	3.47	4.66	6.38
4.92	0.76	4.43	0.69	4.91	2.74	4.86	4.77	4.90	8.54
5.16	0.94	4.65	1.03	5.15	3.85	5.15	6.83	5.14	12.24
5.40	1.58	4.93	1.44	5.39	5.52	5.39	10.27	5.40	19.04
5.64	2.33	5.15	2.12	5.64	8.67	5.64	15.25	5.64	28.10
		5.40	3.23						
		5.64	5.07						

* $[\mathrm{A}]_T = 3.0 \times 10^{-2}$ mol dm^{-3}.

Table 4 Pseudo-first-order rate constants as a function of temperature and pH for the reaction of L-ascorbic acid with $[\mathrm{Co}\{\mathrm{Co(tren)(OH)_2}\}_3]^{6+}$ (conditions as in Table 2)

20.1 °C		25.1 °C*		30.2 °C		35.0 °C		40.1 °C	
pH	$10^2\,k_{obs}/s^{-1}$	pH	$10^2\,k_{obs}/s^{-1}$	pH	$10^2\,k_{obs}/s^{-1}$	pH	$10^2\,k_{obs}/s^{-1}$	pH	$10^2\,k_{obs}/s^{-1}$
4.48	0.24	3.92	0.31	4.46	0.78	4.44	1.39	4.44	3.03
4.68	0.25	4.11	0.41	4.66	0.99	4.64	1.75	4.63	3.30
4.91	0.33	4.32	0.49	4.90	1.39	4.88	2.29	4.86	4.30
5.15	0.47	4.55	0.62	5.13	1.82	5.12	3.41	5.12	6.70
5.38	0.69	4.74	0.66	5.37	2.51	5.35	4.84	5.34	9.28
5.62	0.99	4.98	0.90	5.62	4.02	5.59	7.04	5.58	14.25
		5.20	1.23						
		5.43	1.74						
		5.66	2.70						

* $[\mathrm{A}]_T = 3.0 \times 10^{-2}$ mol dm^{-3}.

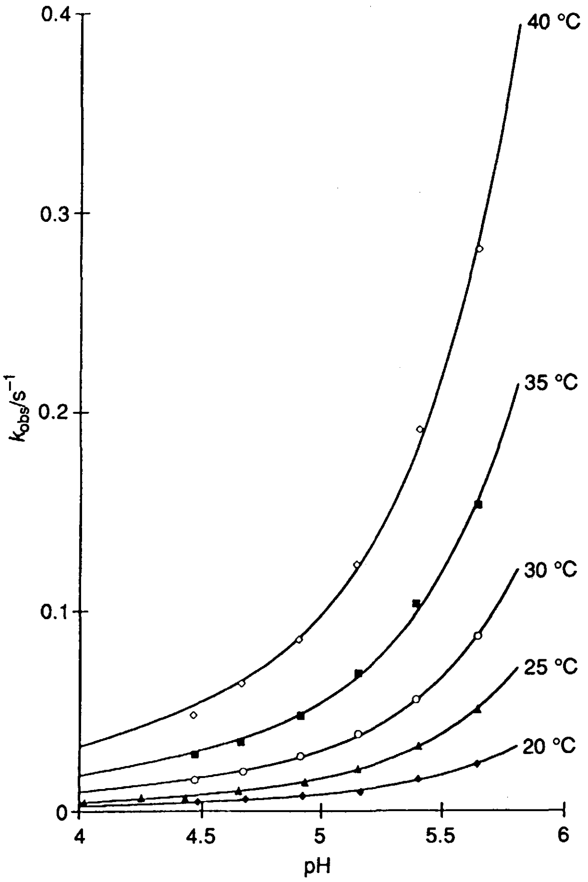


Fig. 1 Variation of k_{obs} with pH for the reaction of L-ascorbic acid with $[\mathrm{Co}\{\mathrm{Co(NH_3)_4(OH)_2}\}_3]^{6+}$

$$2\ \text{radicals} \xrightarrow{\text{fast}} \mathrm{H}_n\mathrm{A}^{n-2} + \mathrm{A} + n\mathrm{H}^+ \qquad (6)$$

$$[\mathrm{Co^{III}}_4] + \text{radical} \xrightarrow{\text{fast}} 3\mathrm{Co^{III}} + \mathrm{A} + n\mathrm{H}^+ \qquad (7)$$

$$\mathrm{Co^{III}} + \text{radical} \xrightarrow{\text{fast}} \mathrm{Co^{II}} + \mathrm{A} + n\mathrm{H}^+ \qquad (8)$$

The acid-dissociation constants for L-ascorbic acid, K_{a1} and K_{a2}, at various temperatures and ionic strengths were taken from the literature.[2,6,7,19–25] At an ionic strength of 0.5 mol dm^{-3} and a temperature of 25.0 °C, K_{a1} and K_{a2} are 1.05×10^{-4} and 7.94×10^{-12} mol dm^{-3} respectively.[5]

The mechanism signifies involvement of the three ascorbate species and expressions (9)–(11) can be derived based on the mechanism.

$$\text{rate} = (k_1[\mathrm{H_2A}] + k_2[\mathrm{HA^-}] + k_3[\mathrm{A^{2-}}])[\mathrm{Co^{III}}_4] \qquad (9)$$

$$= \left[\frac{(k_1[\mathrm{H^+}]^2 + k_2K_{a1}[\mathrm{H^+}] + k_3K_{a1}K_{a2})[\mathrm{A}]_T}{[\mathrm{H^+}]^2 + K_{a1}[\mathrm{H^+}] + K_{a1}K_{a2}}\right][\mathrm{Co^{III}}_4] \qquad (10)$$

$$k_{obs} = \frac{k_1[\mathrm{H^+}]^2 + k_2K_{a1}[\mathrm{H^+}] + k_3K_{a1}K_{a2}}{[\mathrm{H^+}]^2 + K_{a1}[\mathrm{H^+}] + K_{a1}K_{a2}}[\mathrm{A}]_T \qquad (11)$$

At pH $\leqslant$ 3.0 the rate of the reaction was extremely slow and at pH 2.5 there was no significant change in the spectrum after 24 h. This indicates that the pathway involving the undissociated ascorbic acid, $\mathrm{H_2A}$, does not contribute or is extremely slow. In either case, this means that under our experimental conditions equation (11) can be modified to (12).

$$k_{obs} = \frac{k_2K_{a1}[\mathrm{H^+}] + k_3K_{a1}K_{a2}}{[\mathrm{H^+}]^2 + K_{a1}[\mathrm{H^+}] + K_{a1}K_{a2}}[\mathrm{A}]_T \qquad (12)$$

Table 5 Rate (dm^3 mol^{-1} s^{-1}) and activation parameters for the oxidation of L-ascorbic acid by cobalt(III) hexols

Complex	T/°C	k_2	$10^{-5}k_3$	$\Delta H_2^\ddagger$/kJ mol^{-1}	$\Delta S_2^\ddagger$/J K^{-1} mol^{-1}	$\Delta H_3^\ddagger$/kJ mol^{-1}	$\Delta S_3^\ddagger$/J K^{-1} mol^{-1}
NH_3 hexol	20	0.15 ± 0.02	3.96 ± 0.18	103 ± 7	89 ± 22	46 ± 3	19 ± 11
	25	0.22 ± 0.02	5.51 ± 0.09				
	30	0.55 ± 0.06	8.14 ± 0.25				
	35	1.13 ± 0.20	9.52 ± 0.53				
	40	2.16 ± 0.31	14.7 ± 0.65				
en hexol	20	0.20 ± 0.02	3.47 ± 0.16	91 ± 8	51 + 26	41 ± 4	2 ± 13
	25	0.26 ± 0.01	4.26 ± 0.06				
	30	0.65 ± 0.02	6.64 ± 0.09				
	35	1.15 ± 0.08	7.45 ± 0.22				
	40	1.99 ± 0.14	11.0 ± 0.31				
tren hexol	20	0.09 ± 0.01	1.52 ± 0.06	89 ± 2	39 ± 5	51 ± 4	27 ± 14
	25	0.19 ± 0.01	1.98 ± 0.04				
	30	0.33 ± 0.02	3.12 ± 0.08				
	35	0.59 ± 0.04	3.78 ± 0.13				
	40	1.08 ± 0.06	6.26 ± 0.15				

Equation (12) implies that a plot of k_{obs} *versus* $[A]_T$ should result in a straight line with zero intercept. Fig. 1 shows the variation of k_{obs} with pH and temperature and conforms with equation (12).

Over the pH range that the reactions were studied the predominant ascorbate species is the monoanion, HA^-, producing the radical $HA^\bullet$ after electron transfer. The fact that the stoichiometry over this pH range is 1:1 indicates that annihilation of the radical *via* equations (6) and (8) is occurring rather than reaction with the hexol complex as in equation (7). At pH $\geqslant$ 8 the main species involved is the dianion, A^{2-}, which produces the radical anion after electron transfer. The stoichiometry at this pH is 1:2 with respect to ascorbate and complex. This is an indication that annihilation of the radical *via* equation (7) is occurring. This is expected to be facilitated by a high charge contribution arising from the 6+ charged complex and the radical anion.

Previous studies[14,17,26,27] have proposed that the A^{2-} species is approximately six orders of magnitude more reactive than HA^-, and this is confirmed by the rate parameters in Table 5, derived from a non-linear regression analysis of the data in Tables 2–4 using equation (12). The variation in rate constants for the series of complexes is more significant for the pathway (k_3) involving A^{2-}. This is a consequence of the higher charge contribution to the redox process.

The effect of temperature on the reactions can be analysed by means of the activation parameters, derived using Eyring's expression.[28] The results, also summarised in Table 5, indicate that the increase in rate of the A^{2-} relative to the HA^- pathway is enthalpy controlled; with a decrease in the enthalpy of activation by about 50 kJ mol^{-1} for each complex. The rate constant k_2 is more or less constant for the three complexes. This is a consequence of the opposing contributions to the activation energy as a result of the decreasing enthalpy and entropy of activation of the complexes in the order NH_3 > en > tren. Calculations of the free energies of activation, $\Delta G^\ddagger$, from the activation parameters yield almost identical values for the three hexols; approximately 76 and 41 kJ mol^{-1} for the HA^- and A^{2-} pathways respectively. The positive $\Delta S^\ddagger$ is possibly due to solvent rearrangement in the highly charged transition states.[2]

The effect of ionic strength on the rate of the reactions is exemplified by the data in Table 6 for the NH_3 hexol. The ionic strength dependence of the rate constants can be described by the Bronsted limiting equation (13).[2] A plot of

$$\log k_2 = \log k^0{}_2 + 2Z_iZ_jA_2I^{\frac{1}{2}} \qquad (13)$$

log k_{obs} *versus* $I^{\frac{1}{2}}$ gave a straight line with a slope of −2. The negative sign is indicative of a reaction involving two ions of unlike charges.

Table 6 Effect of ionic strength on the rate of the reaction of L-ascorbic acid with $[Co\{Co(NH_3)_4(OH)_2\}_3]^{6+}$ at pH 7.51, 25.1 °C initial [complex] = 5×10^{-4} mol dm^{-3} and $[A]_T = 2.5 \times 10^{-2}$ mol dm^{-3}

I/mol dm^{-3}	k_{obs}/s^{-1}
0.20	25.8
0.30	19.8
0.40	13.4
0.50	10.3

Application of Fuoss theory

The outer-sphere electron-transfer process consists of three steps; formation of the precursor ion-pair complex; irreversible electron transfer and dissociation of the successor complex to yield the reaction products. Of these, the actual electron transfer is rate determining since the precursor formation and product dissociation are both diffusion controlled. The process is illustrated by Scheme 1. The observed second-order rate constant is equal to the composite term $k_{et}K_{os}$. The association constant, K_{os}, can be obtained from the extended Fuoss equation for ion-pair formation;[29] where w_{ij} is the electric work term required to bring the reactants to the contact distance σ ($=r_i + r_j$) in the precursor complex. The work term, from the Debye–Hückel interaction potential to allow for ionic strength effects, can be expressed as[30] in equation (15) where Z_i and Z_j are the charges on the species, e_0 the electronic charge, ε_0 the permittivity of free space, ε the relative permittivity of the medium and χ the reciprocal Debye–Huckel length given by equation (16).[2] At 25 °C ε = 78.4 and $\chi = 3.29\ I^{\frac{1}{2}}$ nm^{-1}. The

$$\text{Red 1} + \text{Ox 2} \overset{K_{os}}{\rightleftharpoons} \{\text{Red 1}\cdot\text{Ox 2}\}$$

$$\{\text{Red 1}\cdot\text{Ox 2}\} \xrightarrow{k_{et}} \{\text{Ox 1}\cdot\text{Red 2}\}$$

$$\{\text{Ox 1}\cdot\text{Red 2}\} \rightleftharpoons \text{Ox 1} + \text{Red 2}$$

Scheme 1

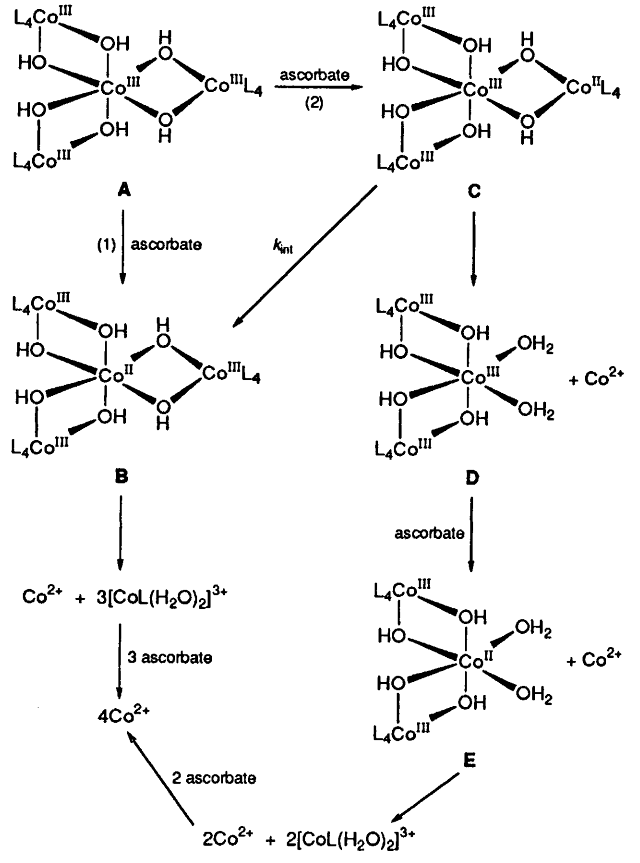
$$K_{os} = \frac{4}{3}\pi\sigma^3N_A\exp(-w_{ij}/RT) \qquad (14)$$

$$w_{ij} = \frac{Z_iZ_je_0{}^2N_A}{4\pi\varepsilon_0\varepsilon\sigma(1 + \chi\sigma)} \qquad (15)$$

$$\chi = (2e_0{}^2\ N_AI/\varepsilon_0\varepsilon k_BT)^{\frac{1}{2}} \qquad (16)$$

Table 7 Rate constants for the actual electron-transfer process in the reactions with L-ascorbic acid at 25 °C

Redox partners	k/dm^3 mol^{-1} s^{-1}	k_{et}/s^{-1}	Ref.
$[Co\{Co(NH_3)_4(OH)_2\}_3]^{6+}]$, HA^-	0.22	2.7×10^{-2}	This work
$[Co\{Co(en)_2(OH)_2\}_3]^{6+}$, HA^-	0.26	3.1×10^{-2}	This work
$[Co\{Co(tren)(OH)_2\}_3]^{6+}$, HA^-	0.19	2.3×10^{-2}	This work
$[Co(NH_3)_4(H_2O)(OH)]^{2+}$, HA^-	5.99	3.5	1
$[Co(en)_2(H_2O)(OH)]^{2+}$, HA^-	0.83	0.43	1
$[Co(tren)(H_2O)(OH)]^{2+}$, HA^-	0.68	0.35	1



Scheme 2

interionic distance σ was calculated using the published value[19] of 0.34 nm for the ionic radius of HA^- and the previously reported radius of 0.47 nm for the en hexol[31] is used for calculations involving the hexols. The calculated rate constants for the actual electron-transfer step, k_{et} for the reactions, shown in Table 7, were determined using the second-order rate constants in Table 5.

Table 7 also contains the values of k_{et} for the reduction of the mononuclear species, $[CoL(H_2O)_2]^{3+}$, by L-ascorbic acid using the previously reported rate constants.[1] The values for K_{os} are approximately 2 and 8 dm^3 mol^{-1} for the mono- and tetranuclear complexes respectively.

It was mentioned above that there are two possible rate-determining steps for the oxidation of ascorbate by cobalt(III) hexols. This is illustrated in Scheme 2. In one pathway, 1, the central cobalt(III) is reduced to cobalt(II), producing the mixed metal complex **B** which then rapidly decomposes to give $[Co(H_2O)_6]^{2+}$ and *cis*-$[CoL(H_2O)_2]^{3+}$. Path 2 involves reduction of one of the outer cobalt(III) moieties to give the mixed-metal complex **C**. Rapid decomposition of **C** with further reduction and decomposition of the intermediates **D** and **E** respectively eventually gives $[Co(H_2O)_6]^{2+}$ and *cis*-$[CoL(H_2O)_2]^{3+}$ as shown. If the reaction occurs by path 2 the intermediate D will be eventually produced. This has an exposed $Co^{III}O_6$ moiety which is expected to be very reactive, and would react with both ascorbate species and radicals. The fact that the stoichiometry is 1 : 2 with respect to hexol and ascorbate at pH ⩾ 8 indicates that for this pH range the rate-determining step involves path 1 and not 2. Previous studies[32,33] have indicated that the intermediate B and closely related complexes are stable over the range pH 6–8. At pH 4.5 the stoichiometry is 1 : 1, hence it is not possible to determine which step is rate determining since the intermediate B is unstable at this pH. However, the results in Table 7 could help in assaying this. The values of k_{et} for the mononuclear complexes are quite close to the values of the second-order rate constants for the reactions with ascorbic acid. Bearing in mind that the mononuclear complexes are very similar to the peripheral cobalt(III) moieties of the hexol complexes, the disparity between the values of k_{et} for the mononuclear complexes and the hexols indicates that the rate-determining step for the reactions of the hexols and ascorbic acid does not involve the peripheral cobalt(III) sites, but rather the central $Co^{III}O_6$.

Acknowledgements

This work was supported by the British Council.

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Received 5*th June* 1995; *Paper* 5/03571F