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# Mechanism of the oxidation of L-ascorbic acid by the pentaammineaquacobalt(III) ion in aqueous solution

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## Summary

The kinetics of oxidation of L-ascorbic acid ($H_2A$) by the mononuclear complex $[Co(NH_3)_5(OH_2)]$ $(ClO_3)_3$ have been studied spectrophotometrically at 490 nm. The mechanism involves single one-electron transfers involving the pentaamminehydroxo complex and the ascorbate anions ($HA^-$ and $A^{2-}$), subsequent formation of ascorbate radicals and $> 90\%$ $Co^{II}$. The appropriate rate law in the $7.00 \leqslant pH \leqslant 8.40$ and $0.005 \leqslant [A_T] \leqslant 0.05$ mol dm$^{-3}$ ranges, has been established as:

$$-d[\text{complex}]/dt = \{(k_3[H^+] + k_4K_{a1})K_2[A]_T[\text{complex}]_T\}/\{([H^+ + K_{a1})([H^+] + K_2)\}$$

The rate is slower at lower pH as the less important reaction $k_1$ ($ROH_2^{3+} + HA^- \longrightarrow$ products) becomes dominant, where R is $(NH_3)_5Co^{III}$. The more significant rate constant $k_4$ ($ROH^{2+} + A^{2-} \longrightarrow$ products) was calculated at 25.7 °C as $(2.7 \pm 0.5) \times 10^2$ dm$^{-3}$ mol$^{-1}$ s$^{-1}$, with $\Delta H^{\#} = 105 \pm 11$ kJ mol$^{-1}$ and $\Delta S^{\#} = 93 \pm 45$ J mol$^{-1}$ $K^{-1}$.

## Introduction

L-Ascorbic acid has become, in recent years, a very popular reductant of numerous metal ions and mononuclear complexes(1–9). These reactions are classified as: (1) outer-sphere electron transfer; (2) inner-sphere electron transfer; or (3) a bridging mechanism where ascorbate is bound at a ligand prior to electron transfer(4).

Tsukahara and Yamamoto(2) reported the outer-sphere electron transfer of cobalt(III) complexes with ligands such as 1,10-phenanthroline and 2,2-bipyridine with ascorbic acid. The same authors described reductions of diaqua and aquahydroxo cobalt(III) tetraazamacrocycles with ascorbate monoanion. In these cases the reactions proceed *via* an OH-bridged mechanism. The polarizability of cobalt(III) in these cases is increased as a result of electron delocalization, so reduction of these complexes by ascorbate, a $\pi$-donor, is facilitated(4).

In this paper we describe the reduction of the mononuclear pentaammineaquacobalt(III) complex with ascorbate for several reasons. In studying the oxidation of L-ascorbic acid by a coordinated chromium(VI) complex, such as the labile pentaamminechromatocobalt(III) ion(10), the pentaamminehydroxo moiety may be involved in the reaction sequence. It is therefore important to know the electron-transfer rate constant between the chromium(VI) ion and L-ascorbic acid(11), and the pentaamminehydroxo ion and L-ascorbic acid, in order to fully explain the complete mechanism between the coordinated chromium(VI) complex and ascorbate. Another facet of this study is to establish whether the hydroxo group is important in the redox process, as was observed in a previous study(4). Furthermore, it was found by Kirby(12) and Sykes(13) that reductants, such as ascorbate, thiosulphate and iron(II), play no part in the reaction of $\mu$-peroxo-bis[pentaamminecobalt(III)] in acid! This additional factor made this study an interesting prospect, as other anomalies could be forthcoming from reaction with this mononuclear system.

## Experimental

### *Materials*

The materials were of analytical or reagent grade and were used as received. The purity of L-ascorbic acid was determined iodometrically(14).

### *Preparation of $[Co(NH_3)_5CO_3]NO_3$*

The complex was synthesized from $Co(NO_3)_2 \cdot 6H_2O$, $(NH_4)_2CO_3$ and concentrated aqueous ammonia as reported in the literature(15). U.v.–vis.: $\lambda_{max}$(nm) 510; $\varepsilon$ (dm$^3$ mol$^{-1}$ cm$^{-1}$) 92.9 [Lit.(16): $\lambda_{max}$ (nm) 510; $\varepsilon$ (dm$^3$ mol$^{-1}$ cm$^{-1}$) 93].

### *Preparation of $[Co(NH_3)_5(OH_2)](ClO)_3$*

This complex was prepared, as outlined in the literature(17), using $HClO_4$ to acidify $[Co(NH_3)_5CO_3]NO_3$. Recrystallization of the pale orange solid was done using warm dilute $HClO_4$. U.v.–vis.: $\lambda_{max}$(nm) 490; $\varepsilon$ (dm$^3$ mol$^{-1}$ cm$^{-1}$) 48.4 [Lit.(17): $\lambda_{max}$ (nm) 490; $\varepsilon$ (dm$^3$ mol$^{-1}$ cm$^{-1}$) 48.6].

### *Stoichiometry*

The redox stoichiometry was obtained by recording absorbances at 490 nm of buffered solutions containing the complex at a fixed concentration while varying added ascorbate, then determining the break in the plot of absorbance *versus* concentration(11). The concentration of $Co^{II}$ from the reaction was determined using Endicott's method(18).

### *Kinetics*

The kinetics were studied at 490 nm using a Pye-Unicam SP8-100 spectrophotometer unit which was connected to a HAAKE KT33 circulatory water bath for maintaining a constant temperature. The ionic strength of the reaction mixtures were maintained using $NaClO_4$, while *tris*–HCl was employed as a buffering medium(19). Reported rate constants were obtained by fitting the absorbance–time data to a STATGRAPHICS computer program(11).

## Results and discussion

### *Stoichiometry*

Table 1 shows data for a 1:1 stoichiometry for the reaction between ascorbate and the pentaammineaquacobalt(III) complex. This was obtained *via* spectro-

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**Table 1.** Stoichiometry of the reaction between L-ascorbic acid and pentaammineaquacobalt(III). $\theta = 25.0\,^{\circ}C$; pH = 7.40 (*tris*–HCl buffer); $I = 0.50\,mol\,dm^{-3}$ ($NaClO_4$); $[complex]_T = 5.0 \times 10^{-3}\,mol\,dm^{-3}$; $\lambda = 490\,nm$

| $[AA]/[Co^{III}]$ | Abs. | $[AA]/[Co^{III}]$ | Abs. |
|---|---|---|---|
| 0.20 | 0.587 | 1.00 | 0.140[a] |
| 0.40 | 0.373 | 2.00 | 0.152 |
| 0.50 | 0.275 | 4.00 | 0.155 |
| 0.80 | 0.155 | 8.00 | 0.108 |

[a] Breakpoint in data occurs at $[AA]/[Co^{III}]$ *ca* 1.00.

photometric titration at 490 nm, where the disappearance of cobalt(III) can be monitored. The quantity of cobalt(II) detected during the reaction was in excess of 90%, indicating quantitative reduction of the cobalt(III).

The stoichiometry obtained was rather unusual as it was expected that ascorbic acid, being a two-electron donor, would reduce two cobalt(III) ions giving a stoichiometry of 0.5:1 [ascorbate: cobalt(III)]. The 1:1 ratio obtained, however, shows that some other reaction involving the radical formed is apparently taking place. One possibility for this reaction is shown in Equation 3. Here, the ascorbate radicals formed react preferentially with each other at a faster rate ($2.8 \times 10^5\,dm^3\,mol^{-1}\,s^{-1}$) than with the cobalt complex(20,21), as was also proposed for the oxidation of ascorbate by hydroxo-bridged dinuclear cobalt(III) complexes(22).

$$HA^- + (NH_3)_5Co(OH)^{2+} \rightarrow 5NH_3 + Co^{II} + OH^- + HA^{\cdot} \quad (1)$$

$$HA^{\cdot} \rightarrow H^+ + A^{\cdot -} \quad (2)$$

$$2A^{\cdot -} \xrightarrow[Co^{II}/O_2]{fast} products \quad (3)$$

This is slower than the rate at which the radical anion reacts with substrates(20), such as cytochrome c ($6.6 \times 10^3\,dm^3\,mol^{-1}\,s^{-1}$), or L-α-ketoglutarate and lactate, which react with rate constants $< 10\,dm^3\,mol^{-1}\,s^{-1}$. No experimental evidence from this work was found which suggests any reaction between ascorbate and the *tris* buffer.

### *Kinetics and mechanism*

The kinetics were studied *via* spectrophotometry over the $0.005 \leqslant [A]_T \leqslant 0.05\,mol\,dm^{-3}$, $7.00 \leqslant pH \leqslant 8.40$, $19.1 \leqslant \theta \leqslant 25.7\,^{\circ}C$ ranges at $0.50\,mol\,dm^{-3}$ in $NaClO_4$. The experimental rate constants increase linearly with increasing ascorbate concentration (constant pH), Figure 1, and with increasing pH at fixed ascorbate concentration (Table 2). The rates show a first-order dependence on the initial concentration of ascorbic acid. The deprotonation constant(23) of the pentaammineaquacobalt(III) ion is $3.98 \times 10^{-7}\,dm^3\,mol^{-1}$, so at high pH the reactive form of the complex is the pentaamminehydroxo species. The known $pK_1$ and $pK_2$ of ascorbic acid are 4.0 and *ca* 12, respectively(12,24), hence the ascorbic acid species, $HA^-$ and $A^{2-}$ are reactive over the pH range chosen for the reaction. Equations showing reactions of the fully protonated ascorbic acid ($H_2A$) are not incorporated in the mechanistic scheme (Equations 4–12), as in acidic environments, where the concentration of $H_2A$ is large, no reaction was observed. The mechanism comprising Equations 4–12 is therefore proposed.

**Table 2.** Pseudo-first order rate constants for the reaction between pentaammineaquacobalt(III) complex and L-ascorbic acid. Effect of pH variation (*tris*–HCl buffer); $I = 0.50\,mol\,dm^{-3}$ ($NaClO_4$); $[A]_T = 8.96 \times 10^{-2}\,mol\,dm^{-3}$; $[complex]_T = 5.0 \times 10^{-3}\,mol\,dm^{-3}$

| pH | $10^3k_{obs}$ ($s^{-1}$) | pH | $10^3k_{obs}$ ($s^{-1}$) | pH | $10^3k_{obs}$ ($s^{-1}$) |
|---|---|---|---|---|---|
| *19.1 °C* | | *21.7 °C* | | *25.7 °C* | |
| 7.00 | 5.23 | 7.18 | 9.70 | 7.01 | 14.7 |
| 7.16 | 5.41 | 7.32 | 9.80 | 7.31 | 15.2 |
| 7.26 | 5.72 | 7.43 | 9.90 | 7.35 | 15.4 |
| 7.40 | 5.87 | 7.53 | 10.0 | 7.45 | 15.9 |
| 7.50 | 6.01 | 7.58 | 10.5 | 7.50 | 16.0 |
| 7.56 | 6.53 | 7.66 | 10.6 | 7.56 | 16.7 |
| 7.65 | 6.57 | 7.74 | 10.7 | 7.74 | 17.5 |
| 7.70 | 6.60 | 7.80 | 10.9 | 7.85 | 18.1 |
| 7.78 | 6.61 | 7.87 | 11.2 | 7.94 | 18.8 |
| 7.85 | 7.06 | 7.95 | 11.2 | 8.01 | 18.9 |
| 7.88 | 7.02 | 7.99 | 11.6 | 8.06 | 19.2 |
| 8.01 | 7.17 | 8.10 | 11.8 | 8.23 | 19.3 |
| 8.10 | 7.23 | 8.16 | 12.1 | 8.33 | 19.9 |
| 8.18 | 7.46 | 8.28 | 12.4 | 8.40 | 20.1 |

| T (°C) | $10^2k_3$ ($dm^3\,mol^{-1}\,s^{-1}$) | $10^{-2}k_4$ ($dm^3\,mol^{-1}\,s^{-1}$) |
|---|---|---|
| 19.1 | 7.3 ± 0.1 | 4.6 ± 0.7 |
| 21.7 | 12.1 ± 0.1 | 3.6 ± 0.4 |
| 25.7 | 19.7 ± 0.2 | 2.7 ± 0.5 |
| | $\Delta H_3^{\#} = 105 \pm 9\,kJ\,mol^{-1}$<br>$\Delta S_3^{\#} = 93 \pm 45\,J\,mol^{-1}\,K^{-1}$ | |

$$H_2A \overset{K_1}{\rightleftharpoons} HA^- + H^+ \quad (4)$$

$$HA^- \overset{K_2}{\rightleftharpoons} A^{2-} + H^+ \quad (5)$$

$$[RCo(OH_2)]^{3+} \overset{K_3}{\rightleftharpoons} [RCo(OH)]^{2+} + H^+ \quad (6)$$

$$[RCo(H_2O)]^{3+} + HA^- \xrightarrow{k_1} Co^{II} + radical \quad (7)$$

$$[RCo(H_2O)]^{3+} + A^{2-} \xrightarrow{k_2} Co^{II} + radical \quad (8)$$

$$[RCo(HO)]^{2+} + HA^- \xrightarrow{k_3} Co^{II} + radical \quad (9)$$

$$[RCo(HO)]^{2+} + A^{2-} \xrightarrow{k_4} Co^{II} + radical \quad (10)$$

$$Co^{II} + radical \xrightarrow{fast} product \quad (11)$$

$$2\ radicals \xrightarrow{fast} product \quad (12)$$

where $R = (NH_3)_5$.

It is expected that because one electron is needed of the reduction of cobalt(III), two single one-electron transfers would take place from ascorbate to the metal ion leading

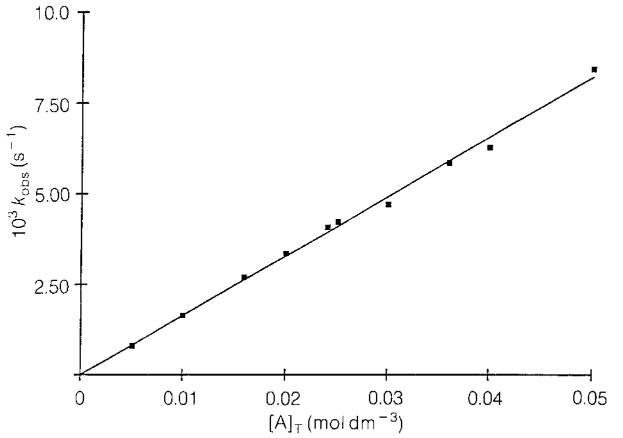

**Fig. 1.** Plot of $k_{obs}$ *versus* $[A]_T$ for the reaction between the L-ascorbic acid and pentaamminеaquacobalt(III) complex. $T = 25\,°C$; $I = 0.5\,M$ ($NaClO_4$); $[complex]_T = 5 \times 10^{-3}\,mol\,dm^{-3}$; pH = 7.3

to the formation of ascorbate radicals. The reactions involving these radical species are known to be fast(1,2,4), although no specific rate constants have been reported for their oxidation by these types of metal complexes.

The ascorbate monoanion concentration was found to be almost constant over the pH range studied. This variation in observed rate constant might therefore be largely due to the increased concentration of the pentaamminehydroxo–cobalt(III) ion, as well as the dianion of ascorbic acid with increasing pH. The $k_1$ and $k_2$ paths contribute very little to the reaction, so the expression obtained by utilizing the $k_3$ and $k_4$ pathways will be of the form shown in Equation 13:

$$k_{obs} = \frac{(k_3[H^+] + k_4K_1)K_2[A]_T}{([H^+] + K_3)([H^+] + K_1)} \tag{13}$$

Upon rearranging, Equation 13 can also be expressed in the form shown below:

$$\frac{k_{obs}([H^+] + K_3)([H^+] + K_1)}{K_2[A]_T} = (k_3[H^+] + k_4K_1) \tag{14}$$

A plot of the left-hand side of Equation 14 *versus* $[H^+]$ produced $k_3$ as the slope with $k_4K_1$ as the intercept (Figure 2). Values for $k_3$ and $k_4$, together with the activation parameters, are listed in Table 2.

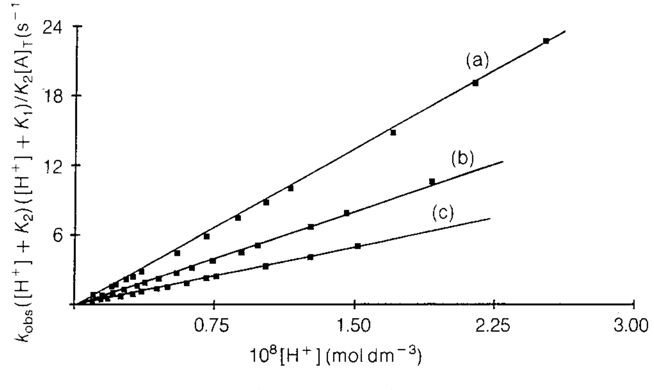

**Fig. 2.** Plot of $k_{obs}([H^+] + K_2)([H^+] + K_{a1})/K_2[A]_T$ *versus* $1/[H^+]$ for the reaction between L-ascorbic acid and pentaammineaquacobalt(III) complex. $T$(°C): (a) 25.0; (b) 21.7; (c) 19.1

**Table 3.** Self-exchange rate constants for various $Co^{III}/Co^{II}$ complexes at 25 °C

| Reaction | $\mu$ (M) | $k_{ex}$ ($M^{-1}\,s^{-1}$) | Ref. |
|---|---|---|---|
| $Co(H_2O)_6^{3+}/Co(H_2O)_6^{2+}$ | 0.5 | 3 | 26 |
| $Co(NH_3)_6^{3+}/Co(NH_3)_6^{2+}$ | 1.0 | $10^{-7}$ | 26 |
| $Co(NH_3)_5(OH)^{2+}/Co(NH_3)_5(OH)^{+}$ | 0.5 | *ca* $1.0 \times 10^{-6}$ | a |
| $Co(NH_3)_4(H_2O)_2^{3+}/Co(NH_3)_4(H_2O)_2^{2+}$ | 0.1 | $1.6 \times 10^{-4}$ | 26 |
| $Co(en)_3^{3+}/Co(en)_3^{2+}$ | 1.0 | $8 \times 10^{-5}$ | 26 |
| $Co(N_4)(H_2O)^{3+}/Co(N_4)(H_2O)^{2+}$ | 0.1 | $3 \times 10^{-5}$ | 4b |
| $Co(dien)_3^{3+}/Co(dien)_3^{2+}$ | 1.0 | $1.9 \times 10^{-4}$ | 26 |
| $Co(phen)_3^{3+}/Co(phen)_3^{2+}$ | 1.0 | $9.5 \times 10^{-2}$ | 26 |
| $Co(N_4)(H_2O)^{3+}/Co(N_4)(H_2O)^{2+}$ | 0.1 | $6 \times 10^{-2}$ | 4c |

[a] This work; [b] $N_4 = Me_6[14]4,11\text{-diene}N_4$; [c] $N_4 = Me_4[14]\text{tetraene}N_4$.

Oxidations of ascorbic acid by most cobalt(III) complexes are often viewed as outer-sphere electron transfer reactions. The Marcus theory for electron-transfer reactions is most useful in calculating the cross-reaction rate constant $k_{12}$ from the equilibrium constant $K_{12}$ for the cross-reaction and the self-exchange rate constants $k_{11}$ and $k_{22}$ for the ascorbic acid and $[Co(NH_3)_5OH]^{2+}$ couples, respectively, according to the following equations(7,25):

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \tag{15}$$

$$\log f = \frac{[\log K^2]}{4[\log(k_{11}k_{22}/10^{22})]} \tag{16}$$

$$\ln K_{12} = nF(E^0_{11} - E^0_{22})/RT \tag{17}$$

Values(8) of $E^0 = 0.71$ V and $k_{11} = 1 \times 10^5\,dm^3\,mol^{-1}\,s^{-1}$, and $E^0 = 0.015$ V and $K_{22} = 2 \times 10^5\,dm^3\,mol^{-1}\,s^{-1}$ were used for the $HA/HA^-$ and $A^-/A^{2-}$ couples, respectively; whilst $E^0$ for $[Co(NH_3)_5OH]^{2+}$ was estimated(26) as 0.33 V. The self-exchange rate constant for $[Co(NH_3)_5OH]^{2+}$ was estimated using the known values for a series of cobalt(III) complexes (Table 3); a value of $1.0 \times 10^{-6}\,dm^3\,mol^{-1}\,s^{-1}$ was chosen, intermediate between the self-exchange values for the $[Co(NH_3)_6]^{3+}/[Co(NH_3)_6]^{2+}$ and $[Co(NH_3)_4(H_2O)_2]^{3+}/[Co(NH_3)_4(H_2O)_2]^{2+}$ couples.

The observed rate constant ($19.7 \times 10^{-2}\,dm^3\,mol^{-1}\,s^{-1}$) exceeds the calculated rate constant of $1.1 \times 10^{-4}\,dm^3\,mol^{-1}\,s^{-1}$ for the $HA^-/[Co(NH_3)_5(OH)]^{2+}$ reaction by a factor of $10^3$, while there is very good agreement between the observed ($2.7 \times 10^2\,dm^3\,mol^{-1}\,s^{-1}$) and calculated ($1.4 \times 10^2\,dm^3\,mol^{-1}\,s^{-1}$) rate constants for the comparable reaction with the ascorbate dianion, $A^{2-}$. This latter case clearly supports an outer-sphere-type model. On the other hand, the disparity between rate constants in the first case may be ascribed partly to the values of parameters, such as the self-exchange rate constants for the $HA/HA^-$ couple, used to calculate the rate of the cross-reaction. Additionally, the ascorbate dianion may be a better outer-sphere reactant than the $HA^-$ species, since it has previously been postulated(4) that reactions with $HA^-$ and some hydroxocobalt(III) species proceed *via* an OH-bridged mechanism. Our findings from this study may be in direct support for the work of those authors, and the reaction in such a case may be more appropriately described as a substitution-limited inner-sphere mechanism(4). Significantly, more energy would be

**Table 4.** Second-order rate constants for the reaction between $Co^{III}$ complexes and L-ascorbic acid at 25 °C

| Redox partners | $k$ ($dm^3 mol^{-1} s^{-1}$) | $\Delta H^{\#}$ ($kJ mol^{-1}$) | $\Delta S^{\#}$ ($J mol K^{-1}$) | Ref. |
|---|---|---|---|---|
| Co($Me_4$[14]tetraeneN$_4$) | $42 \pm 2$<br>$(1.3 \pm 0.1) \times 10^{3a}$ | | | 4 |
| Co($Me_6$[14]4,11-dieneN$_4$) | $3.4 \pm 0.6$<br>$(1.1 \pm 0.1) \times 10^{2a}$ | | | 4 |
| Co(*ms*-$Me_6$[14]aneN$_4$) | $42 \pm 1$<br>$(5.5 \pm 0.1) \times 10^{a}$ | | | 4 |
| Co([14]aneN$_4$) | *ca.* 0<br>$(2.9 \pm 0.6) \times 10^{a}$ | | | 4 |
| $[Co(phen)_3]^{3+}$ | $0.4 \pm 0.07$ | | | 2 |
| $[Co(bpy)_3]^{3+}$ | $0.13 \pm 0.02$ | | | 2 |
| $[Co(en)(phen)_2]^{3+}$ | *ca.* 0 | | | 2 |
| $[Co(NH_3)_5(OH)]^{2+}$ | $(1.97 \pm 0.02) \times 10^{-1}$ | $105 \pm 9$ | $93 \pm 45$ | This work |
| $[Co(NH_3)_6]^{3+}/HA^-$ | 2.7 | $36 \pm 1$ | $-116 \pm 3$ | 26 |
| $[Co(NH_3)_5Cl]^{2+}/HA^-$ | $9 \times 10^{-4}$ | $81 \pm 8$ | $-29 \pm 27$ | 26 |
| $[Co(NH_3)_5Cl]^2/A^{2-}$ | $1.8 \times 10^2$ | $59 \pm 1$ | $-3 \pm 5$ | 26 |
| | $3.4 \times 10^{-4}$ | $81 \pm 6$ | $1 \pm 20$ | 26 |
| $[Co(NH_3)_4(H_2O)_2]^{3+}/HA^-$ | | | | |

[a] Reaction with the hydroxo forms of the complex.

expended in bringing the two reactants together for this kind of interaction.

Tsukahara and co-workers(2,4) have studied the reactions between ascorbate and cobalt(III) complexes containing ligands such as 1,10-phenanthroline, bipyridine and tetraazamacrocycles. These cobalt complexes with $\pi$-conjugated ligands were seen to react quite readily with ascorbic acid. Table 4 shows rate constants of the reaction between ascorbate and some cobalt(III) complexes. The data show the pentaammineaquacobalt(III) complex as having the smallest rate constant. This is because the polarizability of the central cobalt(III) ion is expected to be enhanced with an increase in the extent of electronic delocalization between the cobalt(III) ion and the coordinated ligands. A $\pi$-electron of ascorbic acid can be more easily transferred to those complexes having unsaturated ligands than to the saturated ammine type complexes.

The enthalpy of activation implies that significant energy is required in the attainment of this transition state, while the seemingly high $\Delta S^{\#}$ value supports a poorly organized transition state, or one where bond breaking seems dominant. The $\Delta H^{\#}$ value seems consistent, but the $\Delta S^{\#}$ value is lower compared to those from reactions of L-ascorbic acid with a series of oxidants (Table 4)(26). Although Co—O and Co—N bond cleavage are known to be slow(27), Tsukahara and co-workers(2,4) believe that the $OH^-$ ligand accelerates the dissociation of the *trans* aquo ligand in $[Co(OH)(N_4)(H_2O)]^{2+}$-type complexes. This is in support of a substitution-limited inner-sphere mechanism, which sees the ascorbate anion replacing the $H_2O$ ligand, so effecting reduction of the cobalt(III).

From this study it is not certain if dissociation of the $NH_3$ ligand in the *trans* position is accelerated by the $OH^-$ ligand. If it occurs, the energy requirement for this process might be large. An energetically unfavourable reaction could ensure that the reaction of the pentaamminehydroxo species with, at least, the ascorbate dianion actually proceeds by an outer-sphere electron- transfer mechanism.

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