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Mechanism of oxidation of L-ascorbic acid by the pentaamminechromatocobalt(III) complex ion in aqueous solution‡

Donovan A. Dixon, Tara P. Dasgupta*,† and Novelette P. Sadler

Department of Chemistry, University of the West Indies, Mona, Kingston 7, Jamaica

Oxidation of L-ascorbic acid by pentaamminechromatocobalt(III) nitrate has been investigated over the ranges $6.1 \leqslant pH \leqslant 8.7$, $21.0 \leqslant \theta \leqslant 30.0$ °C, in excess of L-ascorbic acid at a constant ionic strength of 0.50 mol dm^{-3} ($NaClO_4$). Overall the reaction occurs in two distinct stages. The first, involving saturation kinetics, proceeds with an increase in absorbance at wavelengths 350–390 nm. During this stage the pentaamminechromato complex and the ascorbate anion react *via* an outer-sphere mechanism to form an ion pair. The rate equation for this stage is (i)

$$1/k_{obs} = (1/k_5K_4[A]_T) + (1/k_5) \quad (i)$$

with $[A]_T$ being total ascorbate, K_4 and k_5 are the equilibrium constant for adduct formation and first-order rate constant for its decomposition, respectively. At 25.0 °C, k_5 and K_4 have respective values of $(3.5 \pm 0.4) \times 10^{-2}$ s^{-1} and $(8.5 \pm 1.7) \times 10^2$ dm^3 mol^{-1}. The second stage involving a decrease in absorbance at similar wavelengths is the reduction of the free chromium(VI) ion which is postulated to have been formed during the first stage of the reaction. The pseudo-first-order rate constant for this stage can be expressed as in equation (ii) where K_1 and K_6

$$k_{obs} = \frac{(k_7[H^+] + k_8K_6)K_1[A]_T}{([H^+] + K_6)(K_1 + [H^+])} \quad (ii)$$

are the proton-dissociation constants for ascorbate and the hydrogenchromate anion. At 25 °C, the rate constant for oxidation of ascorbate by $HCrO_4^-$, k_7, is 5.15 ± 0.06 dm^3 mol^{-1} s^{-1} while k_8, the corresponding value for oxidation by CrO_4^{2-}, is $(4.6 \pm 1.5) \times 10^{-2}$. Cobalt(III) is reduced to cobalt(II), as >90% cobalt(II) was detected at the end of the second stage of the kinetic reaction. The activation enthalpies lie in the range 20–47 kJ mol^{-1}, and the $\Delta S^{\ddagger}$ values range from −204 J K^{-1} mol^{-1} for the first stage to −50 J K^{-1} mol^{-1} for the k_8 step in the second stage. The mechanism is discussed with respect to the oxidising properties of both the cobalt and chromium centres, and a comparison is also made with the reaction of free chromate ion and L-ascorbic acid.

The formation of complexes of chromium(VI), such as those with aqua transition-metal complexes, has been well documented.[1] Studies have also identified 1:1 chromate esters which can be synthesized from chromium(VI) and oxoanions,[2] equation (1) where $X = CH_3CO_2^-$, $H_2PO_4^-$ or $Cr_2O_7^{2-}$. In the very

$$HCrO_4^- \times X^- + H^+ \longrightarrow XCrO_3^- + H_2O \quad (1)$$

early part of the 20th century some novel chromato complexes were prepared.[3] Among these were the amminechromato cobalt(III) complexes $[Co(NH_3)_5(CrO_4)]^+$ and $[Co(NH_3)_4(CrO_4)]^+$. The kinetics and mechanisms of their formation and subsequent hydrolyses have since been thoroughly investigated.[4,5]

Despite its abundant usage for analytical and preparative purposes, it was discovered that hexavalent chromium showed carcinogenic properties.[6–8] As a result, the reactions of cellular components, including amino acids, ascorbic acid, carboxylic acids and other important low-molecular-weight substrates with chromate have since been researched and documented.[6–10]

It is worthy of note that no previous work has utilised any co-ordinated chromium(VI) ion for similar redox reactions. As a result, its oxidising properties while ligated have remained largely untested. So, in continuing our general investigation of the oxidation of cellular substrates by the chromium(VI) ion, we report in this paper the first study involving the oxidation of L-ascorbic acid by a co-ordinated chromium(VI) ion.

† E-Mail:tara@uwimona.edu.jm

‡ *Supplementary data available* (No. SUP 57240, 3 pp.): stoichiometry data and pseudo-first-order rate constants. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1.

Experimental

Materials

The chemicals were either analytical or reagent grade and used as received. The purity of L-ascorbic acid was determined iodometrically.[11]

Preparation of complexes

Pentaamminecarbonatocobalt(III) nitrate. The complex was prepared according to the established method,[12] and characterised by its UV/VIS spectrum: λ_{max}/nm 510, ε/dm^3 mol^{-1} cm^{-1} 92.9 (lit.,[13] λ_{max}/nm 510, ε/dm^3 mol^{-1} cm^{-1} 93).

Pentaamminechromatocobalt(III) nitrate monohydrate. This complex was prepared from pentaamminecarbonatocobalt(III) as reported previously.[5] UV/VIS data: λ_{max}/nm 540, ε/dm^3 mol^{-1} cm^{-1} 174 (lit.,[4] λ_{max}/nm 540, ε/dm^3 mol^{-1} cm^{-1} 168.4) (Found: N, 24.8; H, 4.75. Calc. for $H_{17}CoCrN_6O_8$: N, 24.7; H, 5.0%).

Product analysis

Upon completion of the reaction between ascorbate and the chromato complex, UV/VIS data of the kinetic solutions revealed that the final product is the chromium(III) bis(ascor-

bate) complex which was also formed as the only product in the reaction between L-ascorbic acid and the chromium(VI) ion.[9] UV/VIS data: $\varepsilon_{590} = 40$ (lit.,[9] 38) and $\varepsilon_{410} = 63$ (sh) $dm^3\ mol^{-1}\ cm^{-1}$ (lit.,[9] 61 $dm^3\ mol^{-1}\ cm^{-1}$) respectively. The kinetic solutions were also analysed for cobalt(II) ions by adding appropriate volumes of acetone and aqueous thiocyanate and comparing the absorption coefficient of the resulting complex with that of a pure sample[14] of $Co(SCN)_2$ at 620 nm where chromium(III) products do not show significant absorption.

Kinetic studies

The kinetics was studied at 370 nm because the chromato complex also has maximum absorption in this region.[4,5] All reactions were conducted using an excess of ascorbic acid at a constant ionic strength of 0.50 mol dm^{-3} ($NaClO_4$). Phosphate–citrate and Tris [tris(hydroxymethyl)methylamine]–HCl were used to maintain the lower and higher pH regions respectively. Rate measurements were done using a Hewlett-Packard 8452A diode-array spectrophotometer, and rate constants were obtained as described previously.[9] The reaction was observed to be biphasic, but the two phases were studied independently. This is possible due to the difference in the rates of the reaction of the two phases, the second being at least an order of magnitude slower than the first.

Results and Discussion

Red-brown pentaamminechromatocobalt(III) reacts with ascorbate to form a green product. Based on UV/VIS data this product was the chromium(III)–ascorbate complex which was also formed in the chromium(VI)–ascorbate reaction under similar experimental conditions.[9] Repetitive scanning of the reaction showed two phases, indicated first by a distinct increase in absorbance followed by a slower decrease. This seems consistent with the formation and decay of an intermediate species.

Stoichiometry

Spectrophotometric titration at 370 nm (Fig. 1) showed the overall stoichiometry [ascorbate:complex] to be 5:2 (SUP 57240). This result suggests that L-ascorbic acid reduces both the cobalt(III) and chromium(VI) according to equation (2),

$$5HA^- + 2[CoCrO_4]^+ + 5H_2O \longrightarrow 3A' + 2HA^{\bullet} + 2Cr^{3+} + 2Co^{2+} + 13OH^- \quad (2)$$

where A′ is the completely oxidised form of L-ascorbic acid. The above stoichiometry is quite consistent with those previously published from separate studies involving first chromium(VI) and ascorbate,[9,10] and secondly between the pentaammineaquacobalt(III) complex ion and ascorbate.[15] The first reaction[9,10] has a stoichiometry of 3:2 (ascorbate:Cr^{VI}), while a 1:1 ratio was obtained in the second study. The combined results from the individual studies therefore produce a ratio of ascorbate:oxidant of 5:2. Despite inherent differences in all the reactions studied, there is good agreement in the final stoichiometries obtained. In a previous publication[15] it was mentioned that the 1:1 stoichiometry for the reduction of the cobalt(III) moiety was due to the radicals reacting rapidly, not with cobalt(III), but with each other at significantly higher rates[16,17] of 2.8×10^5 $dm^3\ mol^{-1}\ s^{-1}$. A similar proposal has been adopted for the oxidation of ascorbate by tetranuclear cobalt(III) complexes.[18]

The analysis for cobalt(II) formed during the reaction produced an average value for the ratio $[Co^{II}]:[Co^{III}]$ of 0.91 ± 0.33, confirming that cobalt(III) in the reactant complex had been reduced by ascorbate.

First phase

The first phase of the reaction was investigated at 370 nm as a function of [ascorbate] over the ranges $0.25 \leqslant [A]_T \leqslant 1.25$ mmol dm^{-1}, $21 \leqslant \theta \leqslant 30$ °C, at an ionic strength of 0.50 mol dm^{-3} ($NaClO_4$) and at pH 8.40 to 9.60. The experimental rate constants increase with increasing [ascorbate] and decreasing pH (Table 1).

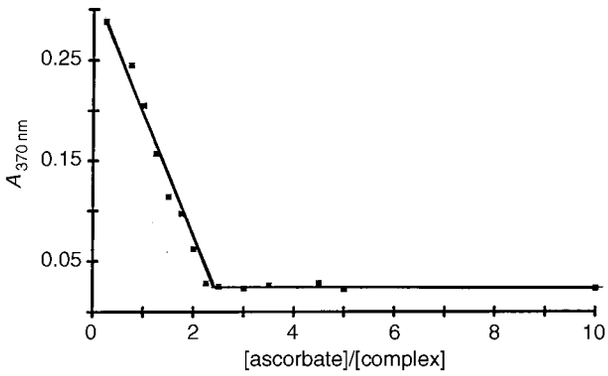


Fig. 1 Stoichiometric plot for the reaction between L-ascorbic acid and the pentaamminechromatocobalt(III) complex. $[complex]_T = 2.0 \times 10^{-4}$ mol dm^{-3}, pH 7.42 (Tris–HCl buffer), $I = 0.50$ mol dm^{-3} ($NaClO_4$)

$$H_2A \overset{K_1}{\rightleftharpoons} HA^- + H^+ \quad (3)$$

$$HA^- \overset{K_2}{\rightleftharpoons} A^{2-} + H^+ \quad (4)$$

$$R_5Co{-}O{-}CrO_3H^{2+} \overset{K_3}{\rightleftharpoons} R_5Co{-}O{-}CrO_3^+ + H^+ \quad (5)$$

$$HA^- + R_5Co{-}O{-}CrO_3^+ \overset{K_4}{\rightleftharpoons} [R_5CoOCrO_3{\cdot}^+HA^-] \quad (6)$$

outer sphere

$$\downarrow k_5$$

$$5R + HCrO_4^- + Co^{2+} + HA^{\bullet}$$

$$HCrO_4^- \overset{K_6}{\rightleftharpoons} CrO_4^{2-} + H^+ \quad (7)$$

$$HCrO_4^- + HA^- \xrightarrow{k_7} Cr^{IV} + A' \quad (8)$$

$$CrO_4^{2-} + HA^- \xrightarrow{k_8} Cr^{IV} + A' \quad (9)$$

$$2\ \text{radicals} \xrightarrow{\text{fast}} H_nA^{n-2} + A' + nH^+ \quad (10)$$

Scheme 1 R = NH_3, A′ = dehydroascorbic acid

A saturation effect was seen in plots of k_{obs} *vs.* [ascorbate], and Scheme 1 is formulated to represent a possible mechanism. Assuming that the complex exists solely[4,5] as the unprotonated form, $[(H_3N)_5CoCrO_4]^+$, at pH ⩾ 8.4, the expression (11) is

$$k_{obs} = \frac{k_5K_4[HA^-]}{1 + K_4[HA^-]} \quad (11)$$

derived from the mechanism in Scheme 1. Substituting for $[HA^-]$ in terms of $[A]_T$ and $[H^+]$ leads to equation (12). Over the

$$k_{obs} = \frac{k_5K_4[H^+][A]_T}{[H^+] + K_2 + K_4[H^+][A]_T} \quad (12)$$

pH range used, $K_2 \ll [H^+]$ (since $K_2 \approx 10^{-12}$ mol dm^{-3}),[9] hence simplification followed by rearrangement of equation (12) results in expression (13). Plots of $1/k_{obs}$ *vs.* $1/[A]_T$ were linear

$$\frac{1}{k_{obs}} = \frac{1}{k_5K_4[A]_T} + \frac{1}{k_5} \quad (13)$$

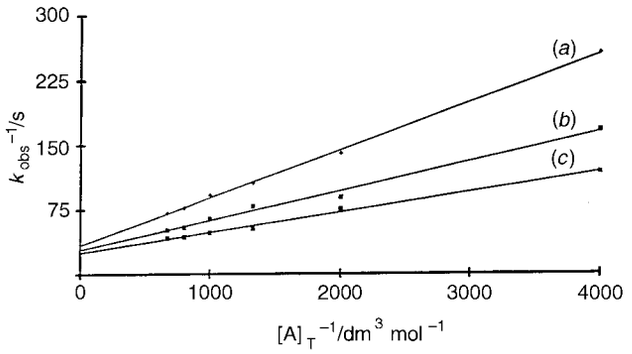


Fig. 2 Plot of $1/k_{obs}$ *vs.* $1/[A]_T$ for the initial phase of the reaction between L-ascorbic acid and the pentaamminechromatocobalt(III) complex at different temperatures: (*a*) 21.0, (*b*) 25.0 and (*c*) 30.0 °C

Table 1 First-order rate constants for the initial reaction between L-ascorbic acid and the chromato complex. Effect of ascorbate concentration. pH 8.40 (Tris–HCl buffer), $I = 0.50$ mol dm^{-3} ($NaClO_4$), [complex]$_T = 2.0 \times 10^{-4}$ mol dm^{-3}

	$10^3 k_{obs}$/s^{-1}		
$10^3[A]_T$/mol dm^{-3}	20.0 °C	25.0 °C	30.0 °C
0.25	3.92		
0.25	1.59[a]		8.52
0.25	0.43[b]	6.03	3.72[a]
0.50	7.17	11.3	13.3
0.75	9.51	12.8	19.2
1.00	10.9	15.7	21.0
1.25	13.0	18.6	23.1
1.50	14.1	19.6	24.0
θ/°C	$10^{-2}K_4$/dm^3 mol^{-1}	$10^2 k_5$/s^{-1}	
20.0	6.6 ± 0.7	2.84 ± 0.23	
25.0	8.5 ± 1.7	3.51 ± 0.38	
30.0	11.6 ± 2.0	3.87 ± 0.32	

$\Delta H_4^\circ = 39 \pm 3$ kJ mol^{-1}, $\Delta H_5^\ddagger = 20 \pm 4$ kJ mol^{-1}, $\Delta S_4^\circ = -57 \pm 11$ J K^{-1} mol^{-1}, $\Delta S_5^\ddagger = -204 \pm 16$ J K^{-1} mol^{-1}

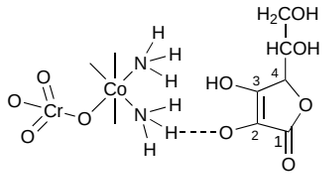
[a] pH 9.00. [b] pH 9.60.

giving $1/k_5$ as intercept and $1/k_5K_4$ as the slope (Fig. 2). The values obtained for K_4 and k_5 are shown in Table 1.

The calculated equilibrium constants are expected to represent adduct formation between ascorbate and the chromato complex. Under the experimental conditions, where the complex exists mainly as the unprotonated form, $[(H_3N)_5CoCrO_4]^+$, its rate of hydrolysis [equation (14)] is slow,[4] since $k_9 < 3.6 \times$

$$[(H_3N)_5CoCrO_4]^+ + H_2O \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} [(H_3N)_5Co(OH)]^{2+} + HCrO_4^- \quad (14)$$

10^{-7} s^{-1} and $k_{-9} = 0.022 \pm 0.073$ dm^3 mol^{-1} s^{-1} at 25 °C, $6.2 \leqslant$ pH $\leqslant 8.5$ and 0.2 mol dm^{-3} Cl^- media. As further confirmation of this, the rate of hydrolysis of the chromato complex was measured independently of the redox reaction at 25 °C, pH 7.4, at an ionic strength of 0.5 mol dm^{-3} ($NaClO_4$). The spontaneous rate of hydrolysis of the complex was measured at $(5.6 \pm 1.4) \times 10^{-4}$ s^{-1}. It is possible that the increased ionic strength could account for the larger rate constant in this work. However, despite the lack of agreement between our value and that of Okumura *et al.*,[4] it is obvious that the hydrolytic pathway is a minor reaction and is not likely to affect subsequent reactions between the pentaamminechromato complex and ascorbate. In the previously published reaction[9] between unbound chromium(VI) and ascorbate anions the rate constants for the reduction of Cr^{VI} are also lower than those for



Scheme 2

the first phase of the reaction between ascorbate and the pentaamminechromatocobalt(III) ion. These observations imply that the reaction being studied in the initial stage is different from the hydrolysis reaction of the chromato complex, and is not due to reduction of the chromium(VI) ion, but supports the idea that the ascorbate monoanion reacts with the pentaamminechromatocobalt(III) ion facilitating formation of the ion pair as two oppositely charged reactants are involved.

Cobalt(III) complexes in general are substitution inert and susceptible to reduction by substrates such as the ascorbate ions,[15,19–22] HA^- and A^{2-}. These reactions are typically described as being outer sphere in nature and take place through formation of an ion pair followed by electron transfer within this assembly. Any reaction between ascorbate and the cobalt(III) in the chromato complex is assumed to proceed *via* a similar mechanism. From the standpoint of electrostatic interactions, the pentaamminechromato complex ion may be viewed as having a dipole moment, with the cobalt(III) portion being the positive end of the molecule. Since the ascorbate is negatively charged, interaction with the cobalt(III) ion may be considered the more favoured possibility, as opposed to interaction with the negatively charged chromium(VI) portion. The former case can lead to the formation of an outer-sphere adduct, as the hydrogens of the ammonia ligands may be ideally suited for hydrogen-bond formation with one of the negatively charged oxygens on the ascorbate anion (Scheme 2).

An alternative pathway is also worthy of consideration, as it has been previously proposed for another type of dinuclear complex. Ascorbate has two reactive oxo groups on carbon atoms 2 and 3, and these may interact simultaneously with the chromium(VI) and cobalt(III) centres, forming an adduct. This idea seems similar to the earlier 'steric match' proposed for the reaction between ascorbate and dinuclear copper(II) complexes.[23]

The first option, based on the kinetic results and electrostatic considerations, is the preferred mechanism for the first phase of this reaction as depicted in Scheme 1. The parameter K_4 represents the outer-sphere association constant for ion-pair formation from the ascorbate anion and the positively charged chromato complex. The k_5 term represents the rate-determining electron-transfer step, which leads to the formation of cobalt(II). The values for k_5 are in agreement with those derived for the oxidation of ascorbate by a series of tetranuclear cobalt(III) complexes (hexols).[8] The increase in absorbance can then be accounted for by the release of the chromium(VI) ion, since cobalt(II) does not absorb significantly at this wavelength, and it is known that chromium(VI) has a larger absorbance than the chromato complex at the wavelength[4,7–9] being studied (Cr^{VI}; $\varepsilon_{370} = 4800$; complex, $\varepsilon_{370} < 3700$ and $\varepsilon_{378} = 2750$ dm^3 mol^{-1} cm^{-1}).

The Marcus cross-relationship may be used to estimate the self-exchange rate constant for the pentaamminechromatocobalt(III) complex ion by utilising equations[24,25] (15)–(18),

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{\frac{1}{2}}W_{12} \quad (15)$$

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4[\ln(k_{11}k_{22}/10^{22}) + (w_{11} + w_{22})/RT]} \quad (16)$$

$$W_{12} = \exp[-(w_{12} + w_{21} - w_{11} - w_{22})/RT] \quad (17)$$

$$w_{ij} = Z_iZ_je^2/D_sa_{ij}(1 + \beta a_{ij}\mu)^{\frac{1}{2}} \quad (18)$$

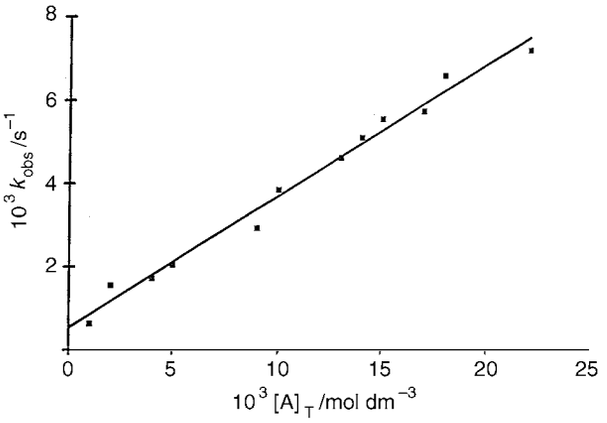


Fig. 3 Plot of k_{obs} *vs.* $[A]_T$ for the oxidation of L-ascorbic acid by the pentaamminechromatocobalt(III) complex. pH 7.40, $\theta = 25.0$ °C and $I = 0.50$ mol dm^{-3}

where k_{11} and k_{22} are the self-exchange rate constants for the chromato complex and ascorbate couples, respectively, k_{12} and K_{12} the rate constant and equilibrium constant for the cross-reaction, Z_i and Z_j the charges of the reacting species, a_{ij} their separation distance, taken to be the sum of the appropriate ionic radii, $\beta = (8Ne^2/1000D_skT)^{\frac{1}{2}}$, D_s is the static relative permittivity and μ is the ionic strength. By using $E° = 0.71$ V and $k_{22} = 1 \times 10^6$ dm^3 mol^{-1} s^{-1} for the HA–HA$^-$ couple, assuming $E° = 0.25$ V for the chromato complex and the inter-ionic distance a_{ij} as the sum of 0.34 and ≈0.45 nm for the ionic radii of HA$^-$ and the chromato complex, respectively, k_{11} was determined as 1×10^4 dm^3 mol^{-1} s^{-1}. This is larger by several orders of magnitude than the self-exchange rate for the pentaammineaquacobalt(III) ion[15] and other mononuclear cobalt(III) complexes.[26,27] No self-exchange rate constants are available in the literature for dinuclear cobalt(III) complexes of this type. The value of k_{11} seems to imply that the cobalt(III) moiety may be more reactive upon co-ordination to the d^0 chromium(VI) ion.[15]

The activation parameter associated with the k_5 pathway may imply some stability in the activated complex generated by this pathway. The negative entropy is indicative of an associative type of reaction, or could implicate the solvent as playing a dominant role. It is not unusual, however, for outer-sphere reactions to exhibit negative entropies of activation as is evident from previous reactions involving mononuclear cobalt(III) sysems.[26,27] The thermodynamic parameters, $\Delta H°$ and $\Delta S°$, also seem consistent with the formation of an ion pair.

Second phase

The kinetics of this reaction was studied over the ranges $6.08 \leqslant pH \leqslant 8.73$, $21.0 \leqslant \theta \leqslant 30.0$ °C and $0.001 \leqslant [A]_T \leqslant 0.022$ mol dm^{-3}, at ionic strength 0.50 mol dm^{-3}. The rate constants increase as the pH decreases (Table 2) and as [ascorbate] increases (SUP 57240). From a plot of k_{obs} *vs.* $[ascorbate]_T$, a slope of 0.32 ± 0.06 dm^3 mol^{-1} s^{-1} and an intercept of $(5.3 \pm 1.2) \times 10^{-4}$ s^{-1} were obtained (Fig. 3). The intercept indicates an ascorbate-independent path, which may be due to spontaneous hydrolysis of the chromato complex under the present experimental conditions. This rate constant is larger than the earlier[4] quoted value ($<3.6 \times 10^{-7}$ s^{-1}), obtained under different conditions, but is in excellent agreement with the rate constant [$(5.6 \pm 1.4) \times 10^{-4}$ s^{-1}] reported in the first phase for the spontaneous hydrolysis studied independently of the second phase.

It is well documented[4,5] that hydrolysis of the chromato complex results in the formation of $HCrO_4^-$ and $[Co(NH_3)_5(OH)]^{2+}$ as indicated in equation (14), and both these species react with ascorbate.[9,15] In aqueous solution it had been shown[9] that the ascorbate monoanion, HA$^-$, is the main reactant under the conditions of this experiment, and the complex may exist as

Table 2 Pseudo-first-order rate constants for the reaction between L-ascorbic acid and the chromato complex. Effect of pH (Tris–HCl buffer); $I = 0.50$ mol dm^{-3} ($NaClO_4$), $[ascorbate]_T = 5.0 \times 10^{-3}$ mol dm^{-3}, $[complex]_T = 2.0 \times 10^{-4}$ mol dm^{-3}

21.4 °C		25.0 °C		29.9 °C	
pH	$10^3 k_{obs}$/s^{-1}	pH	$10^3 k_{obs}$/s^{-1}	pH	$10^3 k_{obs}$/s^{-1}
6.12	15.6	6.22	18.0	6.08	25.5
6.21	14.0	6.34	13.0	6.14	25.4
6.28	13.9	6.42	14.6	6.16	24.9
6.37	12.9	6.61	11.7	6.22	23.1
6.51	10.7	6.69	11.2	6.34	21.9
6.60	9.52	6.79	9.18	6.44	19.5
6.70	8.46	6.94	7.70	6.53	18.7
6.80	7.30	7.05	7.00	6.55	17.6
6.90	6.17	7.10	5.85	6.61	16.3
6.97	5.82	7.15	5.93	6.65	15.1
7.00	5.79	7.22	4.87	6.80	13.4
7.17	3.90	7.31	4.15	6.84	12.6
7.22	3.29	7.34	2.99	6.93	11.1
7.30	2.92	7.48	2.14	6.98	11.2
7.55	1.42	7.58	1.90	7.03	9.59
7.70	1.34	7.66	1.86	7.05	9.37
7.80	1.27	7.78	1.74	7.10	9.21
7.81	1.00	7.85	1.76	7.15	7.64
7.84	0.97	7.91	1.29	7.24	6.01
7.85	0.96	7.98	1.32	7.28	5.83
7.89	0.79			7.31	5.54
7.99	0.76			7.37	4.62
8.03	0.72			7.39	4.87
8.07	0.72			7.42	4.75
8.09	0.70			7.45	4.16
				7.57	3.51
				7.66	3.47
				7.74	3.25
				7.80	2.08

θ/°C	$10^2 k_8$/dm^3 mol^{-1} s^{-1}	k_7/dm^3 mol^{-1} s^{-1}	$10^7 K_6$/mol dm^{-3}
21.4	4.65 ± 1.8	4.58 ± 0.04	3.61 ± 0.10
25.0	4.63 ± 1.5	5.15 ± 0.06	2.83 ± 0.20
29.9	5.50 ± 1.9	6.70 ± 0.05	2.51 ± 0.20

$\Delta H_8^‡ = 47 \pm 9$ kJ mol^{-1}, $\Delta H_7^‡ = 31 \pm 4$ kJ mol^{-1}, $\Delta S_8^‡ = -50 \pm 39$ J K^{-1} mol^{-1}, $\Delta S_7^‡ = -127 \pm 16$ J K^{-1} mol^{-1}

the protonated or unprotonated form. From the proposed mechanism in Scheme 1 equation (19) can be obtained for the

$$k_{obs} = \frac{(k_7[H^+] + k_8K_6)[H^+]K_1[A]_T}{([H^+] + K_6)(K_1K_2 + K_1[H^+] + [H^+]^2)} \quad (19)$$

elementary processes [equations (8) and (9)] which involve oxidation of HA$^-$ by $HCrO_4^-$ and CrO_4^{2-}, respectively. Over the pH range used in this study, and using the known values of the two protonation constants of L-ascorbic acid,[9] the relation $K_1K_2 < K_1[H^+] + [H^+]^2$ is justifiable, hence K_1K_2 may be omitted and upon simplification equation (20) is obtained from which

$$k_{obs} = \frac{(k_7[H^+] + k_8K_6)K_1[A]_T}{([H^+] + K_6)(K_1 + [H^+])} \quad (20)$$

the rate constants k_7 and k_8 can be evaluated. Non-linear regression analyses by the usual method[9,15] produced the best fits (Table 3), while the linear form of equation (16) was used to generate the fits in Fig. 4.

A good fit using equation (20) was directly dependent on the value of K_6. The final form of the rate law [equation (20)] is identical to that used for the chromium(VI) system[9] above pH 5. If free chromate is formed during the course of the reaction, then K_6 represents the proton-dissociation constant for the hydrogenchromate anion. From the analysis, the calculated values of K_6 are smaller than the literature value by a factor of 3–4, less than an order of magnitude. The agreement between

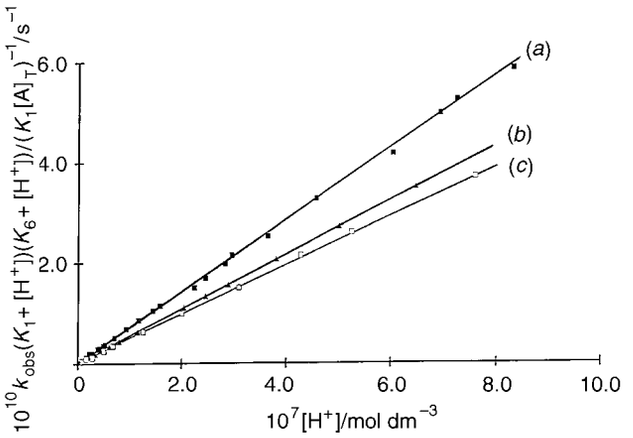


Fig. 4 Plot of $k_{obs}(K_1 + [H^+])(K_6 + [H^+])/K_1[A]_T$ *vs.* $[H^+]$ for the oxidation of L-ascorbic acid by the pentaamminechromatocobalt(III) complex at different temperatures: (*a*) 29.9, (*b*) 25.0 and (*c*) 21.4 °C

the two protonation constants is encouraging, since the latter is calculated from the kinetic results and furthermore was determined in the presence of pentaamminehydroxocobalt(III) which may have caused a slight lowering of K_6.

Oxidations by the chromium(VI) ion are known to proceed through a number of steps including the formation of ester-type intermediates followed by subsequent electron transfers. In this intermediate species substrates such as ascorbate is bound at the chromium centre, generating a five-co-ordinate system the formation of which is pH dependent and provides a low-energy route which facilitates electron-transfer processes *via* an inner-sphere type mechanism. In deriving equation (19) it is assumed that formation of the ester intermediate is rate determining and no appreciable build up of this intermediate occurs, as three single electron transfers leading ultimately to the chromium(III) product are extremely fast.[9]

The $[H^+]$-dependent path, k_7, has the larger rate constant, while k_8 is smaller by a factor of 10^3. Both, however, are smaller than those of the major pathways for the reaction between the free Cr^{VI} ion and ascorbic acid,[9] with k_8 being about two times smaller than the previous value of 0.10 ± 0.02 dm^3 mol^{-1}, which should be construed as good agreement. It was mentioned that during the analysis the value of k_7 was dependent on K_6. The somewhat lower value obtained for k_7 is linked with the reduced value of K_6, the protonation constant of $HCrO_4^-$. In fact, sample calculations indicate that k_7 increases as K_6 increases.

The activation parameters for the k_7 path ($\Delta H_7^{\ddagger} = 31 \pm 4$ kJ mol^{-1}, $\Delta S_7^{\ddagger} = -127 \pm 16$ J K^{-1} mol^{-1}) are not completely different from those for the reaction between the unbound chromium(VI) ion and ascorbate (Table 3), where the corresponding values were $\Delta H^{\ddagger} = 44 \pm 3$ kJ mol^{-1} and $\Delta S^{\ddagger} = -62 \pm 11$ J K^{-1} mol^{-1}. The enthalpies of activation are identical, within experimental error, but a slightly lower entropy of activation is obtained from this study. It is possible that the role of the solvent is more important in this reaction, due to the presence of the positively charged cobalt ions. This could influence constriction of the solvent molecules, leading to a more negative entropy, since the activated complexes are expected to be the same for both sets of reactions.

The foregoing discussion implies that the mechanism proposed is plausible for phase 1 of the reaction. It is observed that both metal centres participate in electron-transfer processes, and it is obvious that chromium(VI) retains its oxidising properties. The ascorbate-induced degradation of the starting complex occurs through electron transfer, not an aquation reaction mediated by ascorbate. The resulting chromium(VI) ion subsequently reacts with ascorbate in a series of one-electron transfer steps in the usual manner, leading to the formation of intermediate chromium-(V) and -(IV) states.[6–10]

Table 3 Summary of rate and activation parameters for the oxidation of the ascorbate anion, HA^-, at 25 °C

Oxidant	Chromato complex[a]	Data[a] from ref. 9
$HCrO_4^-$	$k_7 = 5.15 \pm 0.06$	$k_1 = 59.5 \pm 0.5$
	$\Delta H_7^{\ddagger} = 31 \pm 4$ kJ mol^{-1}	$\Delta H_1^{\ddagger} = 44 \pm 3$ kJ mol^{-1}
	$\Delta S_7^{\ddagger} = -127 \pm 16$ J K^{-1} mol^{-1}	$\Delta S_1^{\ddagger} = -62 \pm 11$ J K^{-1} mol^{-1}
CrO_4^{2-}	$k_8 = (4.6 \pm 1.5) \times 10^{-2}$	$k_2 = 0.10 \pm 0.02$
	$\Delta H_8^{\ddagger} = 47 \pm 9$ kJ mol^{-1}	$\Delta H_2^{\ddagger} = 695 \pm 133$ kJ mol^{-1}
	$\Delta S_8^{\ddagger} = -50 \pm 39$ J K^{-1} mol^{-1}	$\Delta S_2^{\ddagger} = -127 \pm 16$ J K^{-1} mol^{-1}
	$K_6 = 2.83 \times 10^{-7}$ mol dm^{-3} [b]	$K_c = 1.05 \times 10^{-6}$ mol dm^{-3} [b]

[a] All rate constants in dm^3 mol^{-1} s^{-1}. [b] Proton dissociation constant for $HCrO_4^- \rightleftharpoons CrO_4^{2-} + H$.

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