Oxidation of L-Ascorbic Acid by Trisoxalatoferrate(III) in Aqueous Solution. Kinetic and Spectroscopic Evidence for the Formation of an Intermediate Species

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Abstract

Kinetic and spectroscopic evidence is reported for the formation of an intermediate Fe(III) oxalate–ascorbate complex during the oxidation of L-ascorbic acid by trisoxalatoferrate(III). The kinetic data for the formation of the intermediate are characteristic of a substitution-controlled process, and exhibit an inverse acid-concentration dependence. This is followed by a relatively slow innersphere electron-transfer reaction which is independent of pH, ascorbic acid concentration, and ionic strength. A detailed discussion of the kinetic data and a comparison with closely related oxidation reactions are presented.

Introduction

The oxidation reactions of L-ascorbic acid (Vitamin C) are of fundamental interest in biochemical and related processes since L-ascorbic acid (AH_2) has a strong reducing action in aqueous solution. In general it is used as a reducing titrant and as an anti-oxidation agent in the food industry [1, 2]. The oxidation mechanism involves the formation of $AH^{\bullet}$ radicals (as demonstrated by EPR measurements [3–5]) which subsequently produce the oxidation product, L-dehydroascorbic acid. Various groups have studied these oxidation reactions using a wide range of oxidants, including O_2 [6], Pt(IV) [7], Ti(III) [8], Ag(I) [9], Hg(II) [10], Ce(IV) [11], Os(VIII) [12], Ir(IV) [13], Mn(III) [14], Fe(III) [15–17], Co(III) [18, 19], Cu(II) [20, 21] and Ni(III) [22]. In general, it was found that these reactions exhibit a characteristic pH dependence which can be related to the acid-dissociation steps of ascorbic acid and/or the hydrolysis equilibria of the oxidant in those cases where the oxidant is an aquated metal ion. Arguments in favour of outersphere and innersphere electron-transfer mechanisms have been presented, and in a few cases it was possible to detect and identify intermediate species. In our earlier work on the oxidation of ascorbic acid by iron(III) species, we could isolate an intermediate ascorbate complex [17] for the reaction with aquated Fe^{3+} [16]. On the other hand, no intermediate could be detected for the oxidation by $Fe(CN)_6^{3-}$ [15], and this reaction presumably follows an outersphere redox mechanism. In this paper we report our findings for oxidation by $Fe(C_2O_4)_3^{3-}$. Direct kinetic and spectroscopic evidence for the participation of an unstable intermediate species is presented.

Experimental

Materials

$K_3[Fe(C_2O_4)_3]$ was prepared from $FeCl_3$ and $K_2C_2O_4$ as described by Johnson [23]. L-Ascorbic acid and all other chemicals were of analytical reagent grade (Merck), and used without further purification. Stock solutions were prepared with deaerated doubly distilled water and purged with N_2 for *ca.* 30 minutes prior to use. Universal buffer mixtures [24] consisting of phosphoric, acetic and boric acid, and sodium hydroxide were used for all work in the pH range 3.0 to 5.0. The ionic strength of the reaction medium was varied between 0.03 and 0.12 M, and adjusted with $NaClO_4$.

Measurements

pH measurements were performed with a Beckman Expandomatic SS-2 pH meter and a reference electrode filled with NaCl to prevent the precipitation of $KClO_4$. UV–Vis spectra were recorded on a Carry 17 high precision spectrophotometer. Kinetic measurements were performed on a thermostated (±0.1 °C) Durrum D110 stopped-flow instrument as a

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function of [ascorbic acid], $[Fe(C_2O_4)_3^{3-}]$, pH, ionic strength and temperature. An excess of ascorbic acid was used in all cases to ensure pseudo-first-order conditions, and the corresponding rate constants were calculated from the absorbance *versus* time trace on the oscilloscope in the usual way. All reported rate constants are the mean values of at least four determinations and subjected to an average error limit of less than 5%.

Results and Discussion

The oxidation of L-ascorbic acid (AH_2) by $Fe(C_2O_4)_3^{3-}$ leads to the formation of L-dehydroascorbic acid (A) according to the overall reaction in eqn. (1). Similar results were found for the other

$$AH_2 + 2Fe(III) \longrightarrow A + 2H^+ + 2Fe(II) \quad (1)$$

oxidizing agents referred to in the Introduction. The nature of the redox reaction will strongly depend on the actual ascorbic acid/ascorbate species (AH_2, AH^- or A^{2-}) participating in the rate-determining step. The corresponding pK_a values for ascorbic acid are 4.1 and 11.4 [6, 25], which means that the oxidation reaction should exhibit a characteristic pH dependence corresponding to the oxidizing properties of the AH_2, AH^- and A^{2-} species. In general, the reactivity increases in this order [25]. It can therefore be expected that AH_2 will be the major reactive species in strongly acidic medium ($0 < pH < 1$) [14, 26, 27], AH^- in the range $2.5 < pH < 5.5$ [6, 9, 10, 21, 28], and A^{2-} at $pH > 6$ [25].

Preliminary experiments with AH_2 and $Fe(C_2O_4)_3^{3-}$ in the pH range 3 to 5 indicated the rapid formation of a red intermediate, which subsequently decomposed to the reaction products. It was possible to record a spectrum of this species (Fig. 1) during the decomposition process, from which it follows that the species has a maximum absorption at 490 nm. The intermediate produced between AH_2 and Fe^{3+} under similar conditions exhibits a maximum absorption at 550 nm [17], which was ascribed to the formation of $Fe(AH)_2^+$ with AH^- coordinated as a bidentate ligand. This spectral difference suggests that the intermediate in the present study is most probably a mixed oxalate–ascorbate complex of Fe(III). The molar extinction coefficient of this species was determined by measuring the maximum absorbance reached at 490 nm as a function of pH and $[AH_2]_T$ with the aid of the stopped-flow instrument. Throughout this paper, the total ascorbic acid concentration is represented by $[AH_2]_T$ and equals the sum of $[AH_2]$ and $[AH^-]$. The results indicated a maximum formation of the intermediate at pH 4.0, with a molar extinction coefficient of 610 M^{-1} cm^{-1} (see Fig. 2). The rates of the formation

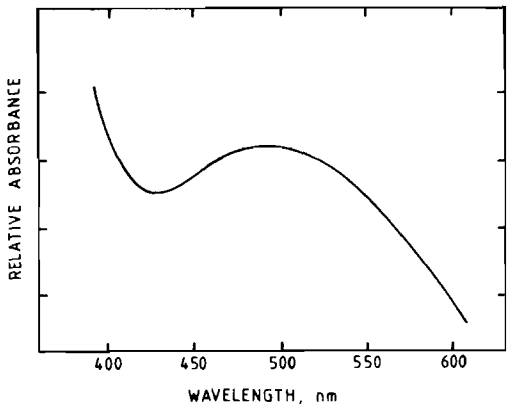

Fig. 1. Absorption spectrum of the intermediate produced during the reaction of L-ascorbic acid and trisoxalatoferrate-(III).

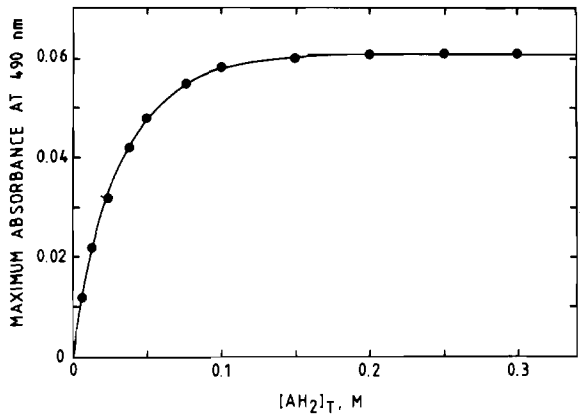

Fig. 2. Plot of maximum absorbance at 490 nm *vs.* total ascorbic acid concentration. $[Fe(III)] = 5 \times 10^{-5}$ M, pH = 4, temperature = 25 °C, optical path length = 2 cm.

and subsequent decomposition reactions are such that they can be separated by selecting different time scales on the stopped-flow instrument.

The formation reaction was followed as a function of pH, $[AH_2]_T$, μ and temperature, and the kinetic data are summarized in Table I. k_{obs} is independent of the [Fe(III)] and increases linearly with $[AH_2]_T$ as indicated in Fig. 3. The pH dependence of the process can be explained in terms of the reaction scheme in (2), in which the produced intermediate is represented by **I**.

$$AH_2 \overset{K_1}{\rightleftharpoons} AH^- + H^+$$

$$Fe(C_2O_4)_3^{3-} + AH^- \overset{k_2}{\longrightarrow} I \quad (2)$$

The corresponding expression for k_{obs} is given in eqn. (3), from which it follows that a plot of k_{obs}^{-1}

TABLE I. Values of k_{obs} as a Function of pH, [Fe(III)], μ, and Temperature for the Formation of the Intermediate Species[a]

pH	$[AH_2]_T \times 10^2$ (M)	μ (M)	Temperature (°C)	k_{obs} (s^{-1})	k_2[b] ($M^{-1}\ s^{-1}$)
3.0	4	0.12	25	1.27	471
3.2				2.14	521
3.4				3.07	500
3.6				4.49	502
3.8				5.77	459
4.0				7.16	427
3.4	4	0.12	25	3.07	500
	6			4.63	502
	8			6.01	489
	10			7.61	495
	12			9.18	498
4.0	4	0.03	25	3.83	228
		0.05		4.89	292
		0.07		5.66	337
		0.09		6.51	388
		0.12		7.16	499
3.4	4	0.12	15	1.34	306
			20	1.88	370
			25	3.07	499
			30	4.91	660
			35	7.02	767
$\Delta H^{\ddagger}$ (kJ mol^{-1})					33.0 ± 2.0
$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})					−82 ± 7

[a][Fe(III)] = 2×10^{-3} M, wavelength = 490 nm. [b]Calculated using eqn. (3) and $K_1 = 7.22 \times 10^{-5}$ M at $\mu = 0.1$ M and 25 °C, see 'Discussion'.

$$k_{obs} = k_2 K_1 [AH_2]_T / (K_1 + [H^+]) \quad (3)$$

versus $[H^+]$ should be linear with intercept $\{k_2 [AH_2]_T\}^{-1}$ and slope $\{k_2 K_1 [AH_2]_T\}^{-1}$. This is indeed the case (Fig. 4), and the resulting values of k_2 and K_1 are 486 $M^{-1}\ s^{-1}$ and 7.22×10^{-5} M, respectively. This value of K_1 is in excellent agreement with the pK_a value quoted above, and demonstrates the validity of the above treatment. Furthermore, these results indicate that there is no significant reaction of $Fe(C_2O_4)_3^{3-}$ with AH_2 under the present experimental conditions. This experimental value for K_1 was used to estimate k_2 under various conditions in Table I. Similarly, from the slope of the plot in Fig. 3, *i.e.* $k_2 K_1 (K_1 + [H^+])^{-1}$ according to eqn. (3), it follows that k_2 has an average value of 497 ± 5 $M^{-1}\ s^{-1}$ at 25 °C and 0.12 M ionic strength, which is in good agreement with the average value obtained from Fig. 4, *viz.* 480 ± 34 $M^{-1}\ s^{-1}$ (Table I).

The ionic strength dependence of k_2 can be obtained under the assumption that K_1 is independent of ionic strength [6, 32]. The resulting values in

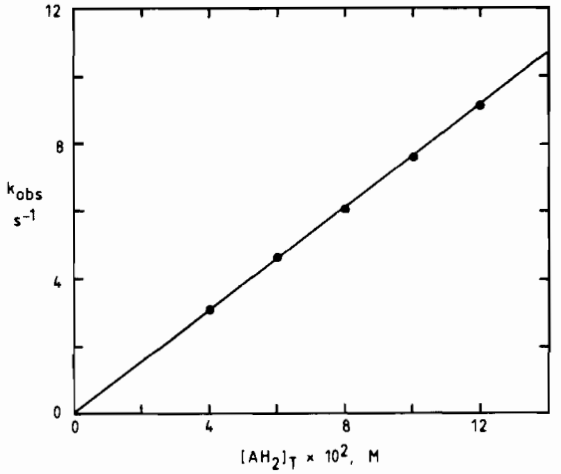

Fig. 3. Plot of k_{obs} *vs.* total ascorbic acid concentration. [Fe(III)] = 2×10^{-3} M, pH = 3.4, $\mu = 0.12$ M, temperature = 25 °C.

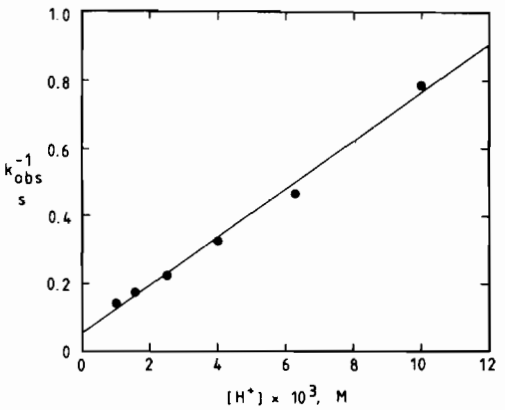

Fig. 4. Plot of k_{obs}^{-1} *vs.* $[H^+]$. [Fe(III)] = 2×10^{-3} M, $[AH_2]_T = 4 \times 10^{-2}$ M; $\mu = 0.12$ M, temperature = 25 °C.

Table I can adequately be described by the Bronsted–Bjerrum eqn. (4), where k_2° is the rate constant at infinite dilution, Z_1 and Z_2 are the ionic charges,

$$\log k_2 = \log k_2^\circ + \frac{2 Z_1 Z_2 A \sqrt{\mu}}{1 + \alpha B \sqrt{\mu}} \quad (4)$$

α is the distance of closest approach of the reacting ions, and A and B are Debye–Hückel constants. For aqueous solutions at 25 °C, $A = 0.509$ $M^{-0.5}$ and $B = 3.29$ nm^{-1} $M^{-0.5}$, such that eqn. (4) modifies to (5) for the present system ($Z_1 = -1$, $Z_2 = -3$). The best fit of the data in Table I was obtained by

$$\log k_2 = \log k_2^\circ + \frac{3.05 \sqrt{\mu}}{1 + 3.29 \alpha \sqrt{\mu}} \quad (5)$$

floating α until a plot of $\log k_2$ *versus* $3.05\sqrt{\mu}(1 + 3.29\alpha\sqrt{\mu})^{-1}$ results in a straight line with unit slope. This is the case for $\alpha = 0.40$ nm (see Fig. 5), from which it follows that $k_2^\circ = 83$ $M^{-1}\ s^{-1}$ at 25 °C. Alternatively, the ionic strength dependence of

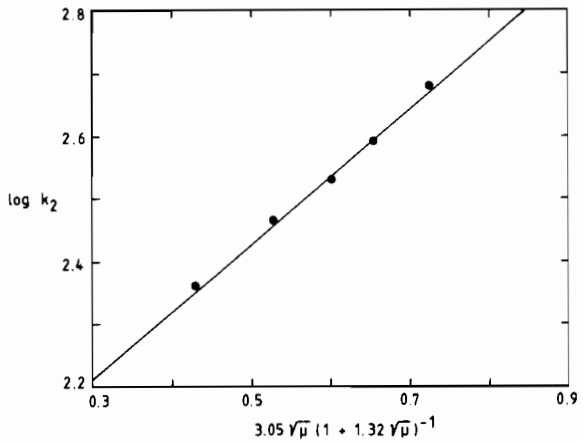

Fig. 5. Plot of log k_2 *vs.* $3.05\sqrt{\mu}(1+1.32\sqrt{\mu})^{-1}$. [Fe(III)] = 2×10^{-3} M, $[AH_2]_T = 4 \times 10^{-2}$ M, pH = 4, temperature = 25 °C.

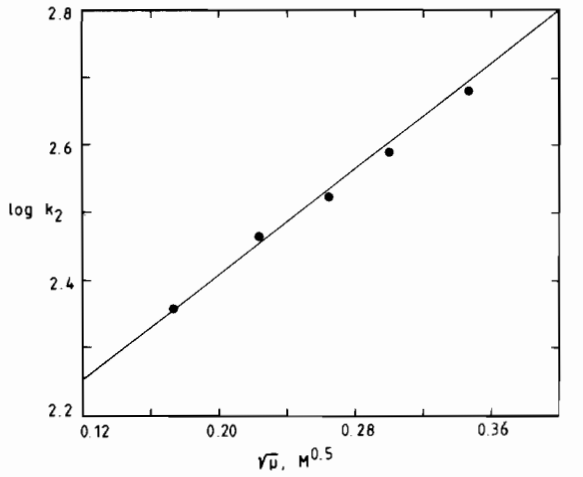

Fig. 6. Plot of log k_2 *vs.* $\sqrt{\mu}$. [Fe(III)] = 2×10^{-3} M, $[AH_2]_T$ = 4×10^{-2} M, pH = 4, temperature = 25 °C.

k_2 can be described by the limiting eqn. (6) applicable at low ionic strength.

$$\log k_2 = \log k_2^\circ + 2Z_1Z_2A\sqrt{\mu} \qquad (6)$$

From the corresponding plot of log k_2 *versus* $\sqrt{\mu}$ (Fig. 6) it follows that $Z_1Z_2 = 1.9$ and $k_2^\circ = 107$ M^{-1} s^{-1}. Both treatments of the ionic strength dependence of k_2 are in line with the rate-determining step suggested in eqn. (2).

The temperature dependence of k_2 was calculated by using eqn. (3) and the following values [6, 32] for $K_1 \times 10^5$ (°C): 4.9 (15); 5.8 (20); 7.2 (25); 9.1 (30); and 11.8 M (35). The corresponding activation parameters are included in Table I. The decomposition reaction of the intermediate was also studied as a function of the same variables, and the kinetic data are summarized in Table II. It follows that this step, eqn. (7), is independent of pH, $[AH_2]_T$, and ionic strength. The temperature dependence of

TABLE II. Values of k_{obs} as a Function of pH, $[AH_2]_T$, μ and Temperature for the Decomposition of the Intermediate Species[a]

pH	$[AH_2]_T \times 10^2$ (M)	μ (M)	Temperature (°C)	k_{obs} (s^{-1})
3.0	4	0–0.04	25	0.123
3.5				0.133
4.0				0.117
4.5				0.123
5.0				0.131
4.5	4	0.03–0.09	25	0.123
	6			0.127
	8			0.128
	10			0.125
	12			0.130
4.5	4	0.03	25	0.123
		0.055		0.126
		0.08		0.121
		0.105		0.122
		0.13		0.124
4.5	4	0.03	15	0.065
			20	0.090
			25	0.125
			30	0.168
			35	0.216
$\Delta H^\ddagger$ (kJ mol^{-1})				42.0 ± 0.9
$\Delta S^\ddagger$ (J K^{-1} mol^{-1})				−120 ± 3

[a][Fe(III)] = 2×10^{-3} M, wavelength = 490 nm.

$$I \xrightarrow{k_3} Fe(C_2O_4)_3^{4-} + AH^\bullet \qquad (7)$$

k_{obs} ($=k_3$) results in the activation parameters included in Table II. The observed kinetic trends underline the intramolecular nature of the process. The rate-determining step, eqn. (7), is presumably followed by a rapid reaction of the $AH^\bullet$ radical with I or $Fe(C_2O_4)_3^{3-}$ to produce the dehydroascorbic acid product, similar to that suggested in the earlier studies [6–22]. In general, the oxidation of the $AH^\bullet$ radical is very fast and rate constants of the order of 10^8 M^{-1} s^{-1} have been reported in the literature [29, 30].

We now turn to a discussion of the data reported in this paper in reference to those reported for closely related systems as summarized in Table III. In general, the oxidation of ascorbic acid proceeds according to a two-term rate law, and much discussion has been focused on the interpretation of the inverse acid-dependent term, which is complicated due to proton ambiguity. The kinetic data for the aquated metal ions as oxidants are usually interpreted in terms of an innersphere mechanism in which substitution is followed by a rapid electron-transfer reaction. In these cases, the observed increase

TABLE III. Rate and Activation Parameters for a Series of Oxidation Reactions of Ascorbic Acid of the General Type[a]:

$$Ox + AH_2 \xrightarrow{k_a} Red + AH^{\cdot} + H^+; \quad Ox + AH^- \xrightarrow{k_b} Red + AH^{\cdot}$$

Ox	k_a (°C) ($M^{-1} s^{-1}$)	k_b (°C) ($M^{-1} s^{-1}$)	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	Reference
Mn^{3+}	6×10^3 (20)		36 ± 7	−50 ± 25	14
$MnOH^{2+}$	5.3×10^4 (20)		30 ± 3	−50 ± 8	14
Fe^{3+} [b]		2×10^6 (20)			16
$Fe(CN)_6^{3-}$	~0	1.2×10^3 (20)			15
$Fe(C_2O_4)_3^{3-}$	~0	5×10^2 (25)	33 ± 2	−82 ± 7	this work
Co^{3+}	2.8×10^2 (25)		63 ± 8	+25 ± 33	18
$CoOH^{2+}$	7.3×10^5 (25)		51 ± 2	−8 ± 8	14, 18
$Co(NH_3)_6^{3+}$	0	2.7 (25)	35.6 ± 0.2	−116 ± 1	19
Cu^{2+}	2.7	2.8×10^3 (20)	45 ± 2	−23 ± 6	21
		40 (25)			20
Ag^+ [c]		42 (35)	40 ± 1	−84 ± 4	9
H_2OsO_5 [c]		1.2×10^3 (30)	59 ± 1	−93 ± 2	12
$IrBr_6^{2-}$	7.4×10^2	4.6×10^7			13
$IrBr_5H_2O^-$	11.1×10^3	13.7×10^7			13
$IrCl_6^{2-}$	4×10^2	2.8×10^7			32
$IrCl_5H_2O^-$	5×10^3	2.7×10^8			32
$IrCl_4(H_2O)_2$	1.2×10^5	3.3×10^9			32

[a]The quoted activation parameters are those for the major reaction path. [b]On the assumption that $k_b \gg k_a$; otherwise $k_a = 2 \times 10^5$ $M^{-1} s^{-1}$. [c]Extrapolated from literature data.

in rate constant with increasing pH is due to the formation of either the more labile metal hydroxo complex or the AH^- species. Oxidation by $Co(NH_3)_6^{3+}$, the Ir(IV) complexes in Table III, and a series of trischelated Fe(III) complexes [32] are typical examples of outersphere electron-transfer processes, and good correlations with the Marcus theory were reported [13]. Along these lines, the oxidation by Fe^{3+} and $Fe(CN)_6^{3-}$ can only be interpreted in terms of an innersphere and outersphere redox process, respectively.

The detection of an intermediate Fe(III) oxalate–ascorbate species is a key aspect of the present study. Two intermediates have been detected before, *viz.* $Fe(AH)_2^+$ and $Cu(AH)^+$ [17, 20, 33]. In the present case the intermediate is probably a mixed complex in which one or both ligands may be coordinated as a monodentate species. The formation of the intermediate exhibits typical kinetics for the substitution of oxalate by AH^-, and the negative $\Delta S^{\ddagger}$ value is in line with an associatively activated process. Furthermore, this reaction is significantly slower than for the oxidation of the aquated Fe(III) species which is known to be extremely labile [16]. Similarly, the more rapid process observed for the $Fe(CN)_6^{3-}$ species is presumably due to an outersphere process, although no activation parameters are presently available to underline this statement [34].

The decomposition of the intermediate is relatively slow, and presumably consists of rate-determining electron transfer followed by rapid release of the $AH^{\cdot}$ species and formation of the trisoxalatoferrate(II) species. The very negative $\Delta S^{\ddagger}$ value is probably due to an increase in electrostriction around the iron centre during the electron-transfer process. Unfortunately, no kinetic data are presently available for the decomposition of the other identified intermediates referred to above, so that no direct comparison is possible. The results of this investigation add a further dimension to the oxidation kinetics of ascorbic acid in that the formation and decomposition of an intermediate species could be detected and studied in detail.

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