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Kinetics and Mechanism of the Oxidation of L-ascorbic acid by Trisoxalatocobaltate(III) in Basic Aqueous Solution

P. MARTINEZ*, J. ZULUAGA

Departemento de Electroquimica, Universidad Autonoma, Madrid-34, Spain

J. KRAFT and R. VAN ELDIK*

Institute for Inorganic Chemistry, University of Witten/Herdecke, Stockumer Str. 10, 5810 Witten, F.R.G.

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Abstract

The kinetics and mechanism of the oxidation of L-ascorbic acid by trisoxalatocobaltate(III) were studied as a function of pH, ascorbate concentration, ionic strength and temperature in a weakly basic aqueous solution. The pH dependence of the process can be ascribed to the oxidation of the doubly deprotonated ascorbate ion for which $k = 20\ \text{M}^{-1}\ \text{s}^{-1}$ at 25 °C, $\Delta H^{\#} = 34 \pm 2$ kJ mol^{-1} and $\Delta S^{\#} = -108 \pm 7$ J K^{-1} mol^{-1}. The results are discussed in reference to literature data for this reaction in weakly acidic medium and for the oxidation by a series of other oxidants.

Introduction

Our general interest in the oxidation mechanism of L-ascorbic acid by various metal reductants [1–7], recently resulted in a detailed study of the oxidation by trisoxalatoferrate(III) [8]. Kinetic and spectroscopic evidence for the formation of an intermediate Fe(III)–oxalate–ascorbate complex was reported, such that the redox process follows an inner-sphere mechanism.

In the present study we investigated the oxidation of L-ascorbic acid by $Co(C_2O_4)_3{}^{3-}$ in basic aqueous solution. Kimura and co-workers [9] studied this reaction in acidic medium ($3.2 \leqslant pH \leqslant 4.7$) and reported kinetic data for the reduction by H_2A and HA^- (H_2A = L-ascorbic acid). The results of this study indicate that A^{2-} is the main reactive species in the range $8 < pH < 10$ and enable a systematic comparison of the reactivity of the protonated and deprotonated ascorbate species.

Experimental

Materials

$K_3[Co(C_2O_4)_3]\cdot 3H_2O$ was prepared according to the method described by Sörensen [10]. 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 min prior to use. Universal buffer mixtures [11] consisting of phosphoric acid, acetic acid, boric acid and sodium hydroxide were used for all work in the pH range 8 to 10. The ionic strength of the reaction medium was varied between 0.05 and 1.0 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 a NaCl solution to prevent the precipitation of $KClO_4$. UV–Vis absorption spectra were recorded on a Cary 17 spectrophotometer. Kinetic measurements were performed on a thermostated (±0.1 °C) Durrum D 110 stopped-flow instrument as a function of ascorbic acid concentration, pH, ionic strength and temperature. The redox process was followed at 600 nm where the $Co(C_2O_4)_3{}^{3-}$ complex has a molar extinction coefficient of $135 \pm 5\ \text{M}^{-1}\ \text{cm}^{-1}$. 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. The reported rate constants are the mean values of at least four determinations and subject to an average error limit of less than 5%. The second dissociation constant of L-ascorbic acid was determined as a function of ionic strength and temperature, using a thermostated Radiometer automatic titrator unit.

Results and Discussion

The oxidation of L-ascorbic acid by $Co(C_2O_4)_3{}^{3-}$ leads rapidly to the formation of L-dehydroascorbic acid (A) according to the stoichiometric eqn. (1).

$$H_2A + 2Co(C_2O_4)_3{}^{3-} \longrightarrow A + 2H^+ + 2Co(C_2O_4)_3{}^{4-} \qquad (1)$$

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*Authors to whom correspondence should be addressed.

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TABLE 1. Rate and Activation Parameters for the Oxidation of L-ascorbic Acid by $Co(C_2O_4)_3^{3-}$ in Weakly Basic Medium[a]

pH	$[H_2A]_T \times 10^2$ (M)	μ (M)	Temperature (°C)	$k_{obs} \times 10^2$ (s^{-1})	k_3[b] ($M^{-1}\ s^{-1}$)
8.5	6	1.0	25	1.0	20.9
8.8				1.9	19.9
9.1				3.8	19.9
9.4				7.6	20.0
9.7				14.7	19.4
10.0				30.6	20.2
9.1	3	1.0	25	1.8	18.9
	4.5			3.0	21.0
	6			3.8	19.9
	9			5.7	20.0
	12			7.6	20.0
10.0	6	0.05	25	0.17	0.35
		0.07		0.33	0.7
		0.09		0.52	1.1
		0.11		0.78	1.6
		0.13		0.95	2.0
9.1	6	1.0	15	1.1	11.5
			20	1.9	14.1
			25	3.8	20.0
			30	6.5	24.1
			35	11.3	29.8
$\Delta H^{\#}$ (kJ mol^{-1})					34 ± 2
$\Delta S^{\#}$ (J K^{-1} mol^{-1})					−108 ± 7

[a] $[Co(III)] = 3 \times 10^{-4}$ M, wavelength = 600 nm. [b] Calculated using eqn. (5) and the K_2 data in Table II.

Similar results were found for other oxidizing agents. This reaction strongly depends on pH [9] since the oxidizing properties of ascorbic acid differ significantly from those of the conjugate base species, *i.e.* HA^- and A^{2-}. The corresponding pK_a values of ascorbic acid are roughly 4 and 11, from which it follows that H_2A will be the major reactive species in strongly acidic medium ($0 < pH < 1$) [10–12], HA^- in the range $2.5 < pH < 5.5$ [6, 9, 13, 14] and A^{2-} at $pH > 6$ [15]. Kimura and co-workers [9] studied reaction (1) in the pH range 3.2 to 4.7 and interpreted their results in terms of the oxidation of H_2A and HA^-. We performed our measurements in the range $8 < pH < 10$ and expected A^{2-} to be the major reactive species although it is only present in very low concentrations under such conditions. More than 90% of the L-ascorbic acid is present as HA^- in this pH range, which should result in an almost pH independent process in the case where HA^- is the major reactive species. The kinetic results in Table I clearly demonstrate that the redox reaction is very pH sensitive in this range, suggesting that A^{2-} is indeed the reactive species.

The kinetic data can be fitted in a quantitative way based on the suggested mechanism in eqn. (2).

$$\begin{aligned}
&H_2A \overset{K_1}{\rightleftharpoons} AH^- + H^+ \\
&AH^- \overset{K_2}{\rightleftharpoons} A^{2-} + H^+ \\
&A^{2-} + Co(C_2O_4)_3^{3-} \xrightarrow{k_3} A^{\dot{-}} + Co(C_2O_4)_3^{4-} \\
&A^{\dot{-}} + Co(C_2O_4)_3^{3-} \xrightarrow{\text{fast}} A + Co(C_2O_4)_3^{4-}
\end{aligned} \qquad (2)$$

It is suggested that the redox partners react in an outer-sphere manner since no evidence for the formation of a stable intermediate, as in the case of oxidation by $Fe(C_2O_4)_3^{3-}$ [8], could be found. The rate of disappearance of $Co(C_2O_4)_3^{3-}$ is given by the rate law in eqn. (3), which can be modified with the aid of eqn. (4) and the pH range of this study to the final expression given in eqn. (5), where $[H_2A]_T$ represents the total concentration of ascorbic acid/ascorbate. According to eqn. (5) a plot of k_{obs} *versus* $[H^+]^{-1}$ at

$$-d[Co(III)]/dt = 2k_3[A^{2-}][Co(III)] = k_{obs}[Co(III)] \qquad (3)$$

$$[A^{2-}] = K_1K_2[H_2A]_T/\{[H^+]^2 + K_1[H^+] + K_1K_2\} \qquad (4)$$

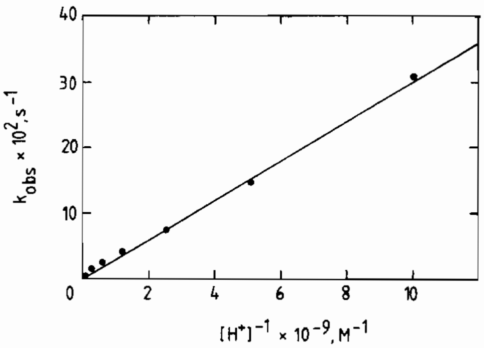

Fig. 1. Plot of k_{obs} *vs.* $[H^+]^{-1}$ for the data in Table I.

$$k_{obs} = 2k_3K_2[H_2A]_T/[H^+] \quad (5)$$

constant $[H_2A]_T$ should be linear with slope $2k_3K_2[H_2A]_T$. The data in Table I is plotted in such a way in Fig. 1 from which it follows that eqn. (5) describes the data quantitatively, with the result that the oxidation of A^{2-} is indeed the major reaction route under the present conditions. The data in Table I also confirms the $[H_2A]_T$ dependence suggested by eqn. (5) and the average value of k_3, *viz.* 20.0 ± 0.5 M^{-1} s^{-1}, is in good agreement with that obtained from the slope in Fig. 1, *viz.* 20.2 ± 0.2 M^{-1} s^{-1}. In order to calculate k_3 it is necessary to have K_2 as a function of temperature and ionic strength. We have therefore performed a systematic potentiometric titration study of L-ascorbic acid, and the values of K_2 are summarized in Table II. These now enable the estimation of k_3 as a function of temperature, and the resulting activation parameters are included in Table I.

TABLE II. The Second Acid Dissociation Constant of L-ascorbic Acid as a Function of Ionic Strength and Temperature

Temperature (°C)	pK_2			
	μ(M) = 0	0.1	0.5	1.0
15	11.9	11.7	11.4	11.2
25	11.5	11.3	11.1	10.9
35	11.2	11.0	10.8	10.6

The ionic strength dependence of k_3 can be obtained from the data in Table I using the values of K_2 given in Table II. A plot of log k_3 *versus* $\sqrt{\mu}$ is linear with an intercept of –1.37 and a slope of 5.6. According to the Bronsted equation the slope presents the product of the charges on the reacting ions, which is indeed close to the value of 6 expected for the mechanism outlined in eqn. (2). With the aid of the k_3^0 (= 2.2×10^{-2} M^{-1} s^{-1}) value obtained from the intercept, we estimated the distance of closest approach (α) of the reacting ions at μ = 1.0 M using the extended Bronsted eqn. (6). The obtained value for

$$\log k_3 = \log k_3^0 + \frac{6.12\sqrt{\mu}}{1 + 3.3\alpha\sqrt{\mu}} \quad (6)$$

α, namely 0.32 nm, is very close to the value of 0.40 nm found for the reaction between HA^- and $Fe(C_2O_4)_3^{3-}$ [8]. It follows that all the kinetic observations underline the validity of the suggested mechanism in eqn. (2).

We now turn to a comparison of the three oxidation pathways of ascorbic acid, *i.e.* via the reaction of

TABLE III. Rate and Activation Parameters for a Selected Series of Oxidation Reactions of Ascorbic Acid

Redox partners[a]	k at 25 °C (M^{-1} s^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (J K^{-1} mol^{-1})	Reference
Mn^{3+}/H_2A	7×10^3	36 ± 7	–50 ± 25	10
$MnOH^{2+}/H_2A$	8×10^4	30 ± 3	–50 ± 8	10
Co^{3+}/H_2A	2.8×10^2	63 ± 8	+25 ± 33	16
$CoOH^{2+}/H_2A$	7.3×10^5	51 ± 2	–8 ± 8	10, 16
$Co(NH_3)_6^{3+}/HA^-$	2.7	36 ± 1	–116 ± 1	4
$Co(C_2O_4)_3^{3-}/H_2A$	1.2×10^{-4}	108 ± 22	+46 ± 61	9
$Co(C_2O_4)_3^{3-}/HA^-$	4.1×10^{-3}	54 ± 4	–109 ± 15	9
$Co(C_2O_4)_3^{3-}/A^{2-}$	20	34 ± 2	–108 ± 7	this work
$Fe(CN)_6^{3-}/HA^-$	729[b]	15.8 ± 0.8	–140 ± 3	17[b]
	1297[c]	12.3 ± 0.5	–144 ± 2	17[c]
$Fe(CN)_6^{3-}/A^{2-}$	2×10^7[d]	17.4 ± 0.4	–47 ± 1	17[d]
$Fe(phen)_3^{3+}/H_2A$	2×10^5	21 ± 1	–73 ± 2	9
$Fe(phen)_3^{3+}/HA^-$	6×10^8	7.7 ± 0.3	–50 ± 1	9
	6×10^8	9 ± 2	–46 ± 7	18

[a] H_2A, HA^- and A^{2-} represent the acidic and basic forms of L-ascorbic acid, respectively. [b] pH = 3. [c] pH = 6. [d] pH = 7.5.

$Co(C_2O_4)_3^{3-}$ with H_2A, HA^- and A^{2-}, as well as the kinetic trends observed for different oxidants. A comparison of the rate and activation parameters for a selected series of oxidation reactions is given in Table III. The results for the oxidation by $Co(C_2O_4)_3^{3-}$ clearly demonstrate the significant enhancement in rate in going from the oxidation of HA^- to A^{2-}. This enhancement is accompanied by a decrease of 20 kJ mol^{-1} in the activation enthalpy, whereas $\Delta S^{\#}$ remains constant within the experimental error limits. This trend indicates that the oxidation by $Co(C_2O_4)_3^{3-}$ is controlled by the activation enthalpy barrier for the electron transfer process. A similar trend is observed for the oxidation of H_2A and HA^- by $Fe(phen)_3^{3-}$. The increase in rate constant of 3 orders of magnitude is accompanied by a significant decrease in $\Delta H^{\#}$. In contrast, the oxidation of HA^- and A^{2-} by $Fe(CN)_6^{3-}$ is entropy controlled since the increase in rate constant of 4 orders of magnitude is accompanied by a significant increase in $\Delta S^{\#}$ and almost no change in $\Delta H^{\#}$. Solvent rearrangement on producing the highly charged transition state must assist the electron-transfer process in the latter case.

The oxidation of H_2A by $Co(C_2O_4)_3^{3-}$ is 9 orders of magnitude slower than the oxidation by $Fe(phen)_3^{3+}$. This can be accounted for in terms of a difference of 80 kJ mol^{-1} in the activation enthalpy. The results for the oxidation of H_2A by $MnOH^{2+}$ and $CoOH^{2+}$ are very similar to those for $Fe(phen)_3^{3+}$, which is in line with the general concept of an outer-sphere electron-transfer mechanism.

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