Inner Sphere Oxidation of L-Ascorbic Acid by Ru(III) Ion and its Complexes in Aqueous Acidic Medium

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Abstract

The kinetics of electron transfer from L-ascorbic acid [H_2A] to oxidants, dichlorotetraaquoruthenium(III) $[RuCl_2(H_2O)_4]^+$, iminodiacetatoruthenium(III) [Ru(III)–IMDA]$^+$ and ethylenediaminetetraacetatoruthenate(III) [Ru(III)–EDTA]$^-$ exhibit a first order dependence both on L-ascorbic acid and oxidants and inverse first order dependence on hydrogen ion concentration. Kinetic, spectroscopic and thermodynamic parameters are reported for the formation of intermediate Ru(III)–ascorbate (1:1) and Ru(III)–chelate–ascorbate (1:1:1) complexes during the oxidation of L-ascorbic acid. The results are interpreted in terms of a mechanism involving a rate-determining inner sphere one electron transfer from L-ascorbic acid to the oxidants used in the present investigation, followed by a subsequent and kinetically rapid transfer of the second electron of ascorbic acid to another molecule of the oxidant. A detailed discussion of the kinetic data, temperature and ionic strength dependence of the oxidation reactions is presented.

Introduction

The biochemical [1–11] and biomedial [12–16] significances of the oxidation of L-ascorbic acid (vitamin C) has stimulated numerous studies of mechanisms of electron transfer in metal complexes. Ascorbic acid is widely used as a reducing agent in chemical and biological systems [1–21] and is finding increasing application as a reductant in photoconversion reactions [22, 23]. It is used as a reducing titrant and as an anti-oxidation agent in the food industry [24, 25]. In the course of many of these studies, ascorbic acid is found to participate in the electron transfer by an outer sphere pathway, in its redox reactions with various metal ions and metal complexes. Inner sphere electron transfer mechanisms for the oxidation of L-ascorbic acid by metal complexes are reported in very few cases [2, 26–28]. In general, it was found that these reactions involve a characteristic pH dependence which can be related to the acid dissociation steps of ascorbic acid. In our laboratories, we have recently characterised ruthenium(III) chloride [29] and its aminopolycarboxylic acid chelates [30]. In this paper, we report our investigations of the reactions between Ru(III) ion, Ru(III)–IMDA and Ru(III)–EDTA with ascorbic acid, under argon. An inner sphere electron transfer mechanism for the oxidation reaction is suggested. The formation of metal ion–ascorbate and metal–chelate–ascorbate intermediates, prior to the actual electron transfer has been well documented from spectroscopic, kinetic and thermodynamic evidences. Ionic strength dependence of the redox reaction is also presented.

Experimental

Materials

All the solutions were prepared using freshly prepared doubly distilled water. L-ascorbic acid was an AR grade sample and was used without further purification. The solution of L-ascorbic acid was freshly prepared for each experiment with deaerated double distilled water. AR grade samples of the disodium salt of EDTA and IMDA obtained from Merck were used in the investigations. Solutions of Ru(III) were prepared in 1 M hydrochloric acid by dissolving the appropriate amount of ruthenium trichloride trihydrate [$RuCl_3 \cdot 3H_2O$] obtained from Johnson Mathey Inc. The concentration of Ru(III) in the solution was estimated spectrophotometrically by the reported method [29–31]. Metal chelates Ru(III)–IMDA and Ru(III)–EDTA were prepared *in situ* by mixing Ru(III) and ligand solutions in a 1:1 molar ratio and the resulting concentrations of the complexes were calculated from the reported stability data [30]. AR grade potassium nitrate was used as a supporting electrolyte to maintain the ionic strength of the solution constant at 0.1 M. All other chemicals used were analytically pure reagents.

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The desired pH of the experimental reaction mixture was adjusted by adding either HCl or carbonate free standard NaOH solution to the reaction mixture.

Measurements

Spectrophotometric experiments were performed by a Beckman model DU-7 high speed UV–Vis spectrophotometer for kinetic and equilibrium measurements. A new peak at 510–515 nm [31] was observed in the case of Ru(III)–ascorbate, Ru(III)–EDTA–ascorbate and Ru(III)–IMDA–ascorbate, immediately after mixing the L-ascorbic acid with the oxidants. This peak is characteristic of the formation of Ru(III)–ascorbate (1:1), Ru(III)–EDTA–ascorbate (1:1:1) and Ru(III)–IMDA–ascorbate (1:1:1) complexes [31]. This peak, which disappeared for dehydroascorbic acid, was used for all kinetic measurements and calculation of stability constants of metal ion–ascorbate and metal–chelate–ascorbate complexes.

The desired temperature (± 0.1 °C) was maintained in the reaction cell with a circulating water bath, while the desired pH was maintained constant at (± 0.01 pH) with a digital pH meter equipped with combined glass and calomel electrodes. The electrode system was calibrated in terms of hydrogen ion concentration by direct titration of HCl and carbonate free NaOH in the acidic and alkaline range. Corrections due to ionic strength were applied in calculating $[H^+]$ from the pH data. The pH values were measured both before and after the oxidation reaction and were found to be reproducible. In order to avoid spontaneous oxidation of ascorbic acid all the experiments were carried out under argon. Thermodynamic and activation parameters corresponding to equilibrium and rate constants were calculated by using Van't Hoff and Arrhenius equations, respectively. The procedures for potentiometric, kinetic, spectrophotometric and thermodynamic studies were described earlier [31].

Results

Stoichiometry

Stoichiometric experiments conducted under argon atmosphere, by maintaining a slight excess of oxidant and by performing spectrophotometric measurements at the proper wavelength (510 nm), indicate the following stoichiometry of the reaction for all the oxidants employed in present study.

$$2Ox + H_2A \longrightarrow 2Red + A + 2H^+ \quad (1)$$

where H_2A and A represent L-ascorbic acid and dehydroascorbic acid, respectively.

Equilibrium Studies

The first and second dissociation constant of L-ascorbic acid determined at 25 °C (μ = 0.1 M KNO_3) are pKa = 3.99 and pK_2a = 11.28. The equilibrium constants (K) for Ru(III)–ascorbate (1:1), Ru(III)–EDTA–ascorbate (1:1:1) and Ru(III)–IMDA–ascorbate (1:1:1) intermediate complexes, calculated spectrophotometrically are 5.99×10^3, 3.31×10^3 and 1.82×10^3 M^{-1}, respectively.

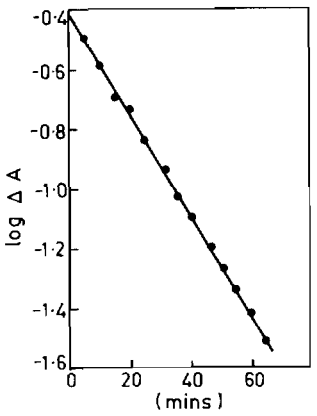

Fig. 1. First order kinetic plot of the oxidation of L-ascorbic acid by $RuCl_2(H_2O)_4^+$ with μ = 0.1 M KNO_3, pH = 2.75; $[RuCl_2(H_2O)_4^+] = 4 \times 10^{-3}$ M at 25 °C.

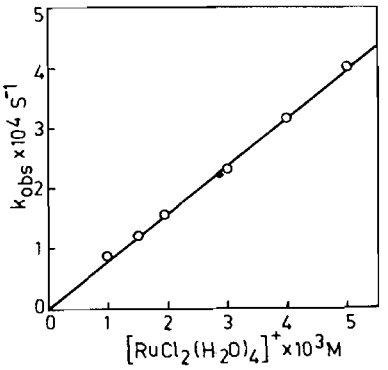

Fig. 2. Plot of $[RuCl_2(H_2O)_4^+]$ *vs.* first order rate constant (k_{obs}) at 25 °C, μ = 0.1 M KNO_3, pH = 2.50 and $[H_2A] = 4 \times 10^{-2}$ M.

Kinetics of Oxidation

In order to examine possible pathways for electron transfer from L-ascorbic acid to metal ion–ascorbate and metal–chelate–ascorbate complexes, a series of kinetic experiments were performed by varying the initial concentration of $[H_2A]_0$, $[oxidant]_0$ and hydrogen ion concentrations, respectively at constant ionic strength and temperature. First order plots (Fig. 1) of log (ΔA) *versus* time, in terms of ascorbic acid concentration, were linear, which indicates that the reaction is first order with respect to [ascorbic acid]. The dependence of first order rate constants k_{obs} on [oxidant] were determined at 25 °C and μ = 0.1 M KNO_3 at constant pH and $[H_2A]_0$. The plot of k_{obs} *versus* [oxidant] (d log k_{obs}/d log[oxidant] = 1) yields a straight line passing through the origin in the

TABLE I. pH and Temperature Dependence for Oxidation of L-Ascorbic Acid by Ru(III), Ru(III)–IMDA and Ru(III)–EDTA at $\mu = 0.1$ M KNO_3, [Oxidant] = 4×10^{-3} M and [Ascorbic Acid] = 4×10^{-2} M

pH	Temperature (°C)	$k_2 \times 10^2$ (M^{-1} s^{-1})		
		Ru(III)	Ru(III)–IMDA	Ru(III)–EDTA
2.00	25	3.05	2.75	2.61
2.25	25	3.80	3.45	3.25
2.50	25	7.85	7.12	5.91
2.75	25	13.90	11.65	10.83
3.00	25	25.73	20.95	18.32
2.00	15	1.95	1.91	1.82
2.00	30	3.65	3.15	3.01
2.00	35	4.20	3.61	3.35

case of all three oxidants. One such plot for the oxidation of ascorbic acid by Ru(III) ion is given in (Fig. 2). Thus the rate of oxidation of L-ascorbic acid is first order in both [ascorbic acid] and [oxidant] following an overall second order kinetics. Over the pH range 2.00 to 3.00, there was a rapid and constant variation in k_{obs} similar to that observed in virtually many of the oxidation studies of ascorbic acid. The kinetic data on pH dependence for ascorbic acid oxidation by Ru(III) ion and Ru(III)–chelates are given in Table I.

Effect of Ionic Strength

In order to investigate the ionic strength effect, kinetic runs were performed at low acidity with increasing addition of supporting electrolyte KNO_3 in the ionic strength range 0.02–0.18 M. Values of the second order rate constants obtained by the variation of ionic strength are listed in Table II.

Thermodynamic Studies

The kinetic data on temperature dependence of the rate of oxidation of L-ascorbic acid are given in Table I. The activation parameters corresponding to the rate of oxidation of L-ascorbic acid by metal ion and metal chelates are listed in Table III with thermodynamic parameters for the dissociation of ascorbic acid and formation of different kinetic intermediate complexes.

Discussion

From the kinetic dependence of the rate of reaction on ascorbic acid and oxidant concentrations, it is clear that the redox reactions depend on the actual ascorbic acid/ascorbate species (H_2A, HA^- or A^{2-}) participating in the rate determining step. The monoanion of ascorbic acid (HA^-) is the major reactive species in the pH range 2.0–5.5 [2, 3, 11]. The mechanism proposed for the oxidation of L-

TABLE II. Ionic Strength Dependence for the Oxidation of L-Ascorbic Acid by Ru(III), Ru(III)–IMDA and Ru(III)–EDTA at 25 °C, pH = 2.75, [Oxidant] = 4×10^{-3} M, [Ascorbic Acid] = 4×10^{-2} M

Oxidant	μ (M)	0.02	0.03	0.05	0.10	0.18
$RuCl_2(H_2O_4)^+$	$k_2 \times 10^2$ (M^{-1} s^{-1})	20.06	19.18	17.35	15.15	14.10
	k'_2 (M^{-1} s^{-1})	3.55	3.39	3.06	2.68	2.49
Ru(III)–IMDA	$k_2 \times 10^2$ (M^{-1} s^{-1})	15.54	15.13	13.48	11.20	10.00
	k'_2 (M^{-1} s^{-1})	2.75	2.68	2.38	1.98	1.76
Ru(III)–EDTA	$k_2 \times 10^2$ (M^{-1} s^{-1})	7.50	8.32	9.33	10.46	12.00
	k'_2 (M^{-1} s^{-1})	1.32	1.47	1.65	1.85	2.12

TABLE III. Activation and Thermodynamic Parameters for Oxidation of L-Ascorbic Acid at $\mu = 0.1$ M KNO_3 in Aqueous Solution

Oxidant	Activation parameters (rate constants)			Equilibrium step	Thermodynamic parameters (equilibrium constant)		
	$\Delta H^{\ddagger}$ (k cal mol^{-1})	$\Delta S^{\ddagger}$ [a] (cal K^{-1} mol^{-1})	$\Delta G^{\ddagger}$ [a] (k cal mol^{-1})		ΔH° (k cal mol^{-1})	ΔS° [a] (cal K^{-1} mol^{-1})	ΔG° [a] (k cal mol^{-1})
$RuCl_2(H_2O)_4^+$	6.01	−53.5	21.95	K_a	6.88	4.7	5.45
Ru(III)–IMDA	5.74	−54.7	22.04	$K^{Ru}_{Ru(HA)}$	3.96	30.52	−5.14
Ru(III)–EDTA	5.47	−56.10	22.18	$K^{RuEDTA}_{RuEDTA(HA)}$	−2.58	7.40	−4.79
Fe(III)–EDTA[b]	4.50	−27.00	12.60	$K^{RuIMDA}_{RuIMDA(HA)}$	−4.06	1.00	−4.33
Fe(III)–HEDTA[b]	5.00	−21.00	11.30				
$Fe(C_2O_4)_3^{3-}$ [c, d]	10.05	−28.70	18.60				

[a]Calculated at 298 K. [b]Ref. 2a. [c]Ref. 28a. [d]$\mu = 0.03$ M $NaClO_4$.

ascorbic acid in the said pH range, therefore, involves the formation of mixed ligand metal–chelate–ascorbate (1:1:1) and metal–ascorbate (1:1) complexes in the pre-equilibrium steps. The Ru(III) complex is reduced in the rate determining step to a Ru(II) species, with a concomitant oxidation of ascorbate to dehydroascorbic acid. It is proposed that the reduction of the first molecule of the Ru(III)L is rate determining with the formation of an ascorbate–semiquinone intermediate. A rapid transfer of electron from the ascorbate semiquinone to another molecule of Ru(III)–L gives dehydroascorbic acid and Ru(II)–L species.

$$H_2A \overset{K_a}{\rightleftharpoons} HA^- + H^+ \quad (2)$$

$$[Ru^{III}L(H_2O)_{6-m}]^{(n-3)-} + HA^- \overset{K_1}{\rightleftharpoons} [Ru^{III}L(H_2O)_{4-m}(HA)]^{(n-2)-} + 2H_2O \quad (3)$$

$$[Ru^{III}L(H_2O)_{4-m}(HA)]^{(n-2)-} \xrightarrow[\text{slow}]{k_1} [Ru^{II}L(H_2O)_{4-m}]^{(n-2)-} + HA^{\cdot} \quad (4)$$

$$[Ru^{III}L(H_2O)_{6-m}]^{(n-3)-} + HA^{\cdot} \xrightarrow{\text{fast}} [Ru^{II}L(H_2O)_{6-m}]^{(n-2)-} + A + H^+ \quad (5)$$

where L = Cl_2, $m = 2$, $n = 2$ for Ru^{III} ion; L = IMDA, $m = 3$, $n = 2$ for Ru(III)–IMDA; L = EDTA, $m = 4$, $n = 4$ for Ru(III)–EDTA; HA^- = ascorbate monoanion; $HA^{\cdot}$ = ascorbate radical.

The rate law describing the oxidation may be written in the form

$$-\frac{d[H_2A]}{dt} = k_1[Ru(III) - L(H_2O)_{4-m}(HA)]^{(n-2)-} \quad (6)$$

where

$$[Ru^{III}L(H_2O)_{4-m}(HA)]^{(n-2)-} = \frac{K_1K_a[H_2A][Ru^{III}L(H_2O)_{6-m}]^{(n-3)-}}{[H^+]}$$

because

$$[HA^-] = \frac{K_a[H_2A]}{[H^+]}$$

hence

$$k_2 = \frac{-d[H_2A]}{dt[H_2A][\text{oxidant}]} = \frac{k_1K_1K_a}{[H^+]} \quad (7a)$$

or

$$k_2 = k'_2K_a/[H^+], \text{ where } k'_2 = k_1K_1 \quad (7b)$$

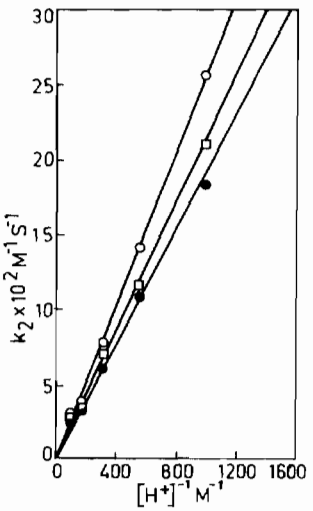

Fig. 3. Acidity dependence of the second order rate constant (k_2) for the oxidation of L-ascorbic acid by Ru(III) ion (○); Ru(III)–IMDA (□) and Ru(III)–EDTA (●) at $\mu = 0.1$ M KNO_3; temp. 25 °C; [oxidant] = 4×10^{-3} M and $[H_2A] = 4 \times 10^{-2}$ M.

The plots of second order rate constant k_2 against inverse hydrogen ion concentration (Fig. 3) pass through the origin for all three oxidants used in present study. This verifies the rate expression (7a) and also suggests that the oxidants are not active for the oxidation of the neutral molecule of ascorbic acid. The rate constants k_1 calculated from slopes of the straight line of Fig. 3 are 4.76×10^{-4} s^{-1}, 4.04×10^{-4} s^{-1} and 3.21×10^{-4} s^{-1} in the case of the oxidants $[RuCl_2(H_2O)_4]^+$, Ru(III)–IMDA and Ru(III)–EDTA, respectively.

It is clear from the ionic strength dependence (Table II) that the rate decreases with ionic strength in the case of the cationic species $[RuCl_2(H_2O)_4]^+$ and $[Ru(III)–IMDA]^+$ whereas in the case of the anionic species $[Ru(III)–EDTA]^-$, the rate increases with increasing ionic strength. The second order rate constant obeys eqn. (8), due to Bronsted–Bjerrum–Christiansen [32].

$$\log k'_2 = \log k_0 + \frac{2Z_AZ_BA\sqrt{\mu}}{1 + B\sqrt{\mu}} \quad (8)$$

where B is a constant which increases with increasing size of the ion, A is also a constant and given more generally by

$$A = \frac{1.82 \times 10^6}{(DT)^{3/2}}$$

D is the dielectric constant of the medium and T is the absolute temperature and k_0 is the rate constant at infinite dilution. Z_A and Z_B are the charges on the two reactant species. At 25 °C, the above equation reduces to

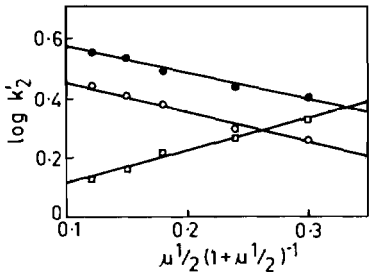

Fig. 4. Ionic strength dependence for the oxidation reaction at 25 °C, [oxidant] = 4×10^{-3} M and [H_2A] = 4×10^{-2} M, (●) $RuCl_2(H_2O)_4^+$; (○) Ru(III)–IMDA; (□) Ru(III)–EDTA.

$$\log k'_2 = \log k_0 + \frac{1.02 Z_A Z_B \mu^{1/2}}{1 + \mu^{1/2}} \qquad (9)$$

because $A = 0.509$ and $B = 1$.

The plots of $\log k'_2$ (Fig. 4) or $\log k_2$ as a function of $\mu^{1/2}(1+\mu^{1/2})^{-1}$ exhibited a slope of (-1) for $RuCl_2(H_2O)_4]^+$ and Ru(III)–IMDA, but, unit (1) positive slope for Ru(III)–EDTA thus confirming that the reaction takes place through the interaction of a -1 and -1 charged species in the case of the oxidant Ru(III)–EDTA and a $+1$ and -1 charge species in the case of the other two oxidants. The ionic strength dependence nicely agrees with the charges on the oxidants and is in line with the rate determining step suggested in step (4). In order to have a clear picture on charges, on oxidants and corresponding kinetic intermediate ascorbate complexes step (3) is written for each oxidant individually in steps (10)–(12). The chloro species of Ru(III) present in our experimental conditions is $[RuCl_2(H_2O)_4]^+$ [29].

$$[RuCl_2(H_2O)_4]^+ + HA^- \underset{Ru}{\overset{K^{Ru}_{Ru(HA)}}{\rightleftharpoons}} [RuCl_2(H_2O)_2(HA)] + 2H_2O \qquad (10)$$
$$Ru(HA)$$

where

$$K^{Ru}_{Ru(HA)} = \frac{[Ru(HA)]}{[Ru][HA^-]}$$

$$[RuEDTA(H_2O)_2]^- + HA^- \underset{RuEDTA}{\overset{K^{Ru(EDTA)}_{RuEDTA(HA)}}{\rightleftharpoons}} [RuEDTA(HA)]^{2-} + 2H_2O \qquad (11)$$
$$RuEDTA(HA)$$

where

$$K^{RuEDTA}_{RuEDTA(HA)} = \frac{[RuEDTA(HA)]}{[RuEDTA][HA^-]}$$

$$[RuIMDA(H_2O)_3]^+ + HA^- \underset{RuIMDA}{\overset{K^{RuIMDA}_{RuIMDA(HA)}}{\rightleftharpoons}} [RuIMDA(HA)(H_2O)] + 2H_2O \qquad (12)$$
$$RuIMDA(HA)$$

where

$$K^{RuIMDA}_{RuIMDA(HA)} = \frac{[RuIMDA(HA)]}{[RuIMDA][HA^-]}$$

The thermodynamic data of electron transfer oxidation of ascorbic acid are given in Table III. This data closely resembles the parameters observed for some Fe(III) complexes [2a, 28a]. From the Table it is clear that the enthalpy of formation (ΔH°) of the Ru(III)–ascorbate complex is endothermic and that of mixed ligand ascorbate complexes of Ru(III)–IMDA or Ru(III)–EDTA are exothermic. The reaction is therefore favoured by the entropy of formation of the complex. The ΔH° for Ru(III)–IMDA–ascorbate complex is 1.5 k cal mol^{-1}, more exothermic than that of the Ru(III)–EDTA–ascorbate complex. The entropy of formation ΔS° for the Ru(III)–EDTA–ascorbate complex is about 6.4 e.u., more positive than that of the Ru(III)–EDTA–ascorbate complex. The difference in the entropies of IMDA and EDTA chelates may be attributed to the number of chelates rings, which are more in EDTA than in the IMDA chelates. The thermodynamic parameters corresponding to Ka show that the dissociation is highly endothermic, the endothermicity depending on the positive value of ΔH° and ΔG°. The entropy of the first proton dissociation is positive, due to hydrogen bonding in the monodissociated species of L-ascorbic acid.

The enthalpies of activation $\Delta H^\ddagger$ of the oxidation of ascorbic acid by the oxidants stated are exothermic and hence the system is enthalpy controlled. The exothermicity of the reaction is countered by the highly negative values of the entropy of activation $\Delta S^\ddagger$. The entropies become more negative in going from Fe(III) to Ru(III). The free energy of activation $\Delta G^\ddagger$ for oxidation of L-ascorbic acid by Ru(III) ion, Ru(III)–IMDA and Ru(III)–EDTA is almost the same which indicates that an identical mechanism is operative for these oxidants.

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