

Kinetics of Oxidation of L-Ascorbic Acid by Cobalt(III) Complexes

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(Received 12th September, 2000, revised 19th May, 2001)

Summary: Kinetics of L-ascorbic acid oxidation by cobalt(III) complexes were studied using stopped-flow spectrophotometry in aqueous solution at 25°C. Kinetics measurements were run under pseudo-first order conditions in which the concentration of ascorbic acid is between one and two orders of magnitude greater than that of the oxidant. Cobalt(III) complexes of urea, $C_2O_4^{2-}$, H_2O , acac, EDTA, NH_3 , en, phen, and NO_2^- , were used to study the ligand effect on ascorbic acid oxidation rate; it is found that the rate of oxidation is first order with respect to both ascorbic acid and oxidizing agents. Results show that the rate of oxidation depends inversely on both the ligand's size and its strength in the spectrochemical series.

Introduction

Electron transfer reactions of transition metal complexes are important in coordination chemistry. These reactions have been widely studied by different methods, including: stopped-flow spectrophotometry, chemical analysis of products, and the use of radioactive and stable isotope tracers. Discussion of these methods, along with much of the data produced in this field, have been discussed elsewhere [1]. The oxidation of ascorbic acid (Vitamin C) is of great importance since it has interesting biological and chemical properties. Ascorbic acid is a lactone with a 2,3-ene-diol group and is so effective as a reducing agent. Its oxidation has wide application in analytical chemistry. Moreover, the reactivity of the ene-diol group has been utilized in a number of organic syntheses. Of particular interest, in the context of transition metal chemistry, is the fact that L-ascorbic acid forms chelates with metal ions; the structures of these chelates species are deduced from spectroscopic studies and is generally believed that a five-member ring with the ene-diol part of the molecule is formed [2].

Several studies dealing with the kinetics of oxidation of ascorbic acid with various oxidizing agents have appeared in the literature [3-8]. Banerjee *et al* [3], reported the kinetics of reduction of nickel(IV) and nickel(III) oxime-imine complexes by ascorbic acid. Oxidation of L-ascorbic acid by hexacyanoferrate(III), in strongly acidic media over a wide range of acidity, was reported by Leal *et al* [4]. Davies [5], investigated extensively the reaction of L-ascorbic acid with several transition metal

complexes. The kinetics and mechanism of the reaction of aqueous iron(III) with ascorbic acid was studied by Jordan *et al* [6]. Kinetics and thermodynamic studies of the oxidation of ascorbic acid by hexacyanoferrate(III) ion in acidic medium were done by Martins *et al* [7]. A theoretical study on the mechanism of oxidation of L-ascorbic acid to dehydroascorbic acid, was investigated by *ab initio* MO calculations [8]. Fabian and Vaneldik [9] reported the temperature and pressure effects on the kinetics of the bromate ions-L-ascorbic acid and iodide ions-L-ascorbic acid clock reaction. However, the effect of the nature of the ligand in a transition metal complex on the rate of oxidation of ascorbic acid has not been studied before.

Recently, the kinetics of oxidation of some amino acids by transition metal complexes has been reported [10]. In addition, the effect of the ligand in a transition metal complex on the rate of oxidation of cysteine has also been reported [11].

In the present work, we report results dealing with the kinetics of oxidation of L-ascorbic acid by cobalt(III) complexes in aqueous solutions at 25°C, using stopped-flow spectrophotometry. Ligands of various sizes and various electron donating/accepting abilities were prepared and were employed in the oxidation processes (Table 1). The kinetics were studied under pseudo-first order conditions, in which the concentration of ascorbic acid was between one and two orders of magnitude greater than that of the oxidant. The observed rate of the reaction was

determined by following the change in the concentration of the oxidizing agent, photomerically, with time, The effect of the nature of the ligand in the Co(III) complex on the rate of ascorbic acid oxidation is presented.

Results and Discussion

Generally, oxidation of ascorbic acid (AAH) leads to the formation of dehydroascorbic acid as shown below [5]:



With transition metal complexes, oxidation of ascorbic acid is believed to give the dehydroascorbic acid dimer [12], as shown below



Estimation of residual oxidant suggested that 2 moles of ascorbic acid (AAH) consume 2 moles of the cobalt(III) complex, $[\text{Co}^{\text{III}}\text{L}_n]^{m+}$, such that

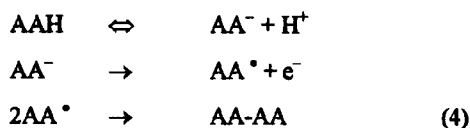


where n is the number of ligands (L) around cobalt(III) and m is the charge on the cobalt(III)-L complex.

The rate of the reaction is given by

$$\text{Rate} = k [\text{AAH}]^a [(\text{CoL}_n)^{m+}]^b \quad (3)$$

where k is the reaction rate constant and a and b are the orders of the reaction with respect to the concentration of AAH and $(\text{CoL}_n)^{m+}$, respectively. It was found that the rate is dependent on the first power of both the concentrations of substrate and oxidant, i.e., $a = b = 1$, in agreement with previous studies [10,11]. Since cobalt(III) complexes are all one-electron oxidants, the oxidation of ascorbic acid would give a radical intermediate, and the following mechanism is proposed:



the second step being the rate-determining step.

At pseudo-first order conditions, where $[\text{AAH}] \gg [(\text{CoL}_n)^{m+}]$, the concentration of ascorbic acid is essentially constant throughout the reaction. The reaction rate is then given by

$$\text{Rate} \approx -\frac{d[(\text{CoL}_n)^{m+}]}{dt} = k_{\text{obs}} [(\text{CoL}_n)^{m+}] \quad (5)$$

where k_{obs} is the observed rate for the reaction, given by

$$k_{\text{obs}} = k [\text{AAH}] \quad (6)$$

where k is the second-order rate constant, in units of $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$

For a first-order dependence of the reaction's rate on $[(\text{CoL}_n)^{m+}]$, the experimental absorbance-time data pairs were fit to the exponential function:

$$A_t = (A_0 - A_\infty) \exp(-k_{\text{obs}} t) + A_\infty \quad (7)$$

where A_t is the absorbance of the cobalt(III) complex at time t through the reaction, A_0 and A_∞ are the initial and the final absorbance of the complex. The products of the oxidation reaction are usually colorless (or don't absorb at the selected wavelength at which the reaction is monitored). Therefore, $A_\infty \approx 0$, and the experimental results fit the simple equation

$$A_t = A_0 \exp(-k_{\text{obs}} t) \quad (8)$$

The value of k_{obs} (in s^{-1}) can be obtained from a plot of $\ln[A_t]$ versus time. From equation 6, a plot of k_{obs} versus $[\text{AAH}]$ gives the value of the second-order rate constant, k . Kinetics results for the oxidation of ascorbic acid by various cobalt(III) complexes are shown in Table 1.

Table-1: Rates of Oxidation of Ascorbic Acid by Various Co(III) Complexes In Aqueous Medium At 25°C, pH = 7.0, and Ionic Strength = 0.50 Mol dm^{-3} .

Complex Ion	Ligand	k ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)
$[\text{Co}(\text{urea})_6]^{3+}$	urea	2.1×10^3
$[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$	$\text{C}_2\text{O}_4^{2-}$	1.5×10^3
$[\text{Co}(\text{H}_2\text{O})_6]^{3+}$	H_2O	3.0×10^2
$[\text{Co}(\text{NH}_3)_6]^{3+}$	NH_3	1.9×10^2
$[\text{Co}(\text{NO}_2)_6]^{3-}$	NO_2^-	6.2×10^{-1}
$[\text{Co}(\text{en})_3]^{3+}$	en	4.0×10^{-3}
$[\text{Co}(\text{acac})_3]$	acac	3.2×10^{-3}
$[\text{Co}(\text{phen})_3]^{3+}$	phen	2.7×10^{-3}
$[\text{Co}(\text{EDTA})]^-$	EDTA	Very slow

• Estimated error in rates is $\pm 5\%$.

Table 1 reveals that the rate constant for the oxidation of ascorbic acid varies widely with the type of ligand in cobalt(III) complex. For outer-sphere reactions, like those studied in the present work [1,10,11], the rate of electron transfer in a complex: $(\text{CoL}_n)^{m+} + e^- \rightarrow (\text{CoL}_n)^{(m-1)+}$, should depend on the nature of the ligand in addition to many other factors (such as the match of energy levels of the two reactants and the solvation of the two reactants); different ligands cause different polarizabilities to the metal ion. Thus, the nature of the ligand determines the ability of the electron(s) to tunnel through the complex to reduce the metal ion, i.e. the electrode potential of the complex. The presence of different ligands in the complex causes different electrode potential for Co^{3+} reduction. There are two reasons that affect the reduction potential of the Co^{3+} complex ion. *First*: ligands with π electrons (π -donors or π -acceptors) provide better pathways for tunneling, and hence facilitate the reduction process. Therefore, it is expected that redox reaction rate should be faster with π -electrons ligand than with σ -donor ligands, or ligand with no extra lone pairs and no low-lying antibonding orbitals. However, the rate of electron transfer through ligands with strong π acceptor effect, like NO_2^- , is expected to be slower than the transfer rate through weaker π -acceptor ligands or π -donor ligands. The presence of vacant π^* in strong π -acceptor ligands makes electron transfer harder. This is due to the possibility of the electron getting "trapped" or "captured", momentarily, in the vacant π^* of the ligand. This is unlikely to occur in electrons "rich" π , or σ -donor ligands. Due to the possibility of back bonding, strong π -acceptors are also strong ligands. For ligands used in the present work (Table 1), the order of their strength in the spectrochemical series is as follows: urea \langle $\text{C}_2\text{O}_4^{2-}$ \langle H_2O \langle acac \langle EDTA \langle NH_3 \langle en \langle phen \langle NO_2^- . According to crystal field theory, for an octahedral symmetry, the d-orbitals split into t_{2g} and e_g orbitals. The magnitude of splitting, Δ_o , depends on the ligand's strength. For a strong ligand with high Δ_o , the donated electron, from ascorbic acid, goes to the higher energy e_g orbitals. This should be more difficult and less probable to occur than donation to the lower energy t_{2g} orbitals for weak ligand. Therefore, one can conclude that the electrode potential of the metal ion becomes less positive, hence the redox rate decreases as the ligand strength in the spectrochemical series increases, which explains the drop in the reaction rate constant

for the first five complexes as presented in Table 1. However, the behavior of the last four complexes in Table 1 can be explained by the size factor discussed below.

It should be noted that at the concentrations used for the kinetics measurements, it is likely for the cobalt(III) complexes of urea and $\text{C}_2\text{O}_4^{2-}$ to undergo dissociation in the aqueous solution; replacement of one ligand by one or two water molecule(s) may occur to give $[\text{Co}(\text{urea})_5(\text{H}_2\text{O})]^{3+}$ and $[\text{Co}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$, respectively. It is also likely that $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ will undergo dissociation to give $[\text{Co}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$. However, these dissociation processes neither change the trend in the ligand strength nor change its correlation with the reaction rate.

The *second* factor that affects the reduction potential of Co^{3+} , and hence the rate of the redox reaction, is the size of the ligand. Table 1 shows that, among donor or acceptor ligands, the rate of the reaction decreases as the size of the ligand increases. The rate is slower for complexes with large size and bulky ligands, such as EDTA and phen, which makes electron tunneling through it *relatively* slow. As mentioned above, the rate of reduction of the metal ion in the complex depends on the ability of the electron to tunnel through the ligand. The probability of an electron to tunnel through the ligands is a quantum mechanical property, which can be calculated from time-dependent perturbation theory. The transition probability of an electron to pass through a potential barrier between two molecules in the gas phase is given by [13]

$$P(t) = \sin^2(2\pi H_{12}t/h) \quad (9)$$

where t is time, h is Planck's constant and H_{12} is the exchange integral, or the interaction energy, between the initial state orbital described by the wave function ϕ_1 and the final state orbital described by the wave function ϕ_2 . It is given by

$$H_{12} = \int \phi_1 \hat{H} \phi_2 d\tau \quad (10)$$

where \hat{H} is the Hamiltonian of the transferring electron. The interaction energy depends on the extent to which the orbitals centered on the two interacting particles overlap with each other. In solutions, electronic transfer between two particles will be hindered by the presence of solvent molecules

because such molecules prevent the extension into space of the orbitals on the exchanging particles. Moreover, the ligands of a complex ion will act as good insulating groups for electrons and orbitals of the central metal ion. The electron tunneling theory developed by Weiss [14] and by Marcus, Zwolinski, and Eyring [15] gives considerable insight into the electron transfer process in solution. As a result, the tunneling of electron in solution is related to the extension in space of the orbitals in connection with gas-phase transfer process. The probability of transfer for an electron leaking through a potential energy barrier across the ligand around the central metal ion is given by the Gamow equation [16].

$$\kappa = \exp\{- (8\pi d/3h)[2m(U-W)]^{1/2}\} \quad (11)$$

where κ is known as the transmission coefficient, U is the height of the potential barrier, W is the kinetic energy of the electron, m is the electron mass, and d is the width of the barrier at the height of penetration. As an approximation one may consider U to represent the potential of an electron moving in the coulomb field of two ions. Therefore, U is given by the coulomb equation

$$U = \frac{q_1 q_2}{Dd} - \frac{eq_1}{Dx} - \frac{eq_2}{D(d-x)} \quad (12)$$

where q_1 and q_2 are the charges of each of the ions (the cobalt(III) complex and ascorbic acid, respectively), D is the dielectric constant of the solvent, and x is the distance the electron has to travel from the electron donor (ascorbic acid) to the center of the electron acceptor (cobalt(III)). This distance depends on the size of the ligand around the central metal ion.

The net charge on ascorbic acid, q_2 , is zero. Therefore, equation (12) reduces to the simple form

$$U = -\frac{eq_1}{Dx} \quad (13)$$

The rate constant, $k(T)$, for electron transfer is given by the transition state theory [17] as

$$k(T) = \kappa \frac{kT}{h} e^{-\Delta G^\ddagger/kT} \quad (14)$$

where T is the reaction temperature, k is the Boltzmann's constant, and ΔG^\ddagger is the free energy change at the activated complex.

Equations (11), (13) and (14) show that as size of the ligand in the complex increases, transmission coefficient and hence the rate constant decreases. This explains the drop in reaction rate constant for the last four complexes in Table 1. This finding is in agreement with previous results reported earlier [11].

In conclusion, the rate of oxidation of ascorbic acid by various cobalt(III) complexes was found to depend inversely on both the strength of the ligand in the complex and its size. The effect of the size was found to be predominant.

Experimental

Preparation and characterization of cobalt(III) complexes

Ascorbic acid (minimum assay 99%) and Co(III) complexes of $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ and $[\text{Co}(\text{acac})_3]$ with minimum assay of 98% and 95%, respectively, were purchased from BDH. Co(III) complexes were purified by double recrystallization to minimum purities of 99%. The other Co(III) complexes used in the study (Table 1) were prepared as described in the literature [18]. The complexes were characterized by various physical and spectroscopic methods: the existence of Co(III) was confirmed by Mössbauer room temperature measurements using a ^{57}Co source with a spectrometer driven in the constant acceleration mode, interfaced to a PC-based multichannel analyzer. The percentage of cobalt in complexes was determined by atomic absorption using Spex Model Alpha 4 spectrometer. Elemental analyses for the complexes were performed by Butterworth Laboratories, UK. Results of elemental analysis are summarized in Table 2.

Kinetic measurements

Freshly prepared aqueous solutions of the desired concentrations of complexes and of ascorbic acid were used for the kinetic measurements. The measurements were carried out using a Hi-Tech Scientific Model SF-61 stopped-flow spectrophotometer. The reaction was monitored by following the decrease in absorbance of the cobalt(III) complex with time at a predetermined wavelength; this wavelength was determined by

Table-2: Results of Elemental Analysis of Different Co(III) Complexes.

Complex	C	H	Found (Calculated) %		Cl	Na	K
			N	Co			
[Co(urea) ₆]Cl ₃	13.8 (13.7)	4.7 (4.6)	31.6 (32.0)	11.0 (11.2)	20.1 (20.3)		
K ₃ [Co(C ₂ O ₄) ₃]. 3H ₂ O	14.7 (14.6)	1.0 (1.2)		11.7 (11.9)			24.1 (23.7)
[Co(acac) ₃]	50.9 (50.6)	5.6 (5.9)		16.7 (16.6)			
[Co(phen) ₃](ClO ₄) ₃ . H ₂ O	47.3 (47.1)	3.0 (2.9)	9.0 (9.2)	6.6 (6.4)	11.8 (11.6)		
Na[Co(EDTA)]. 5H ₂ O	26.1 (26.1)	4.5 (4.8)	6.0 (6.1)	12.9 (12.8)		5.3 (5.0)	
Na ₃ [Co(NO ₂) ₆]			20.6 (20.8)	14.5 (14.6)		16.8 (17.1)	
[Co(en) ₃]ClSO ₄	6.6 (6.5)	6.4 (6.5)	22.5 (22.7)	16.0 (15.9)	9.7 (9.6)		
[Co(NH ₃) ₆]Cl ₃		6.6 (6.7)	31.2 (31.4)	22.2 (22.0)	40.0 (39.8)		

recording the absorption spectral curves, for the cobalt(III) complex and for its mixture with ascorbic acid after the completion of the reaction, using Diode-Array UV/VIS spectrophotometer (HP Model 8453). The reaction progress was monitored at the wavelength of maximum absorbance difference between the absorption of the complex and that for the mixture; the monochromator of the stopped-flow apparatus was tuned to this wavelength and the reaction rate was measured. All oxidation reactions were studied under pseudo-first order conditions. The concentrations of the ascorbic acid used [0.01 – 0.1 mol dm⁻³] were chosen to be 1-2 orders of magnitude larger than that of the cobalt(III) complexes [0.001 – 0.01 mol dm⁻³]. For both Co(acac)₃ and [Co(phen)₃](ClO₄)₃.H₂O the lower concentration limits were used due to their low solubilities in water. The ionic strength of the solutions was kept constant at 0.50 mol dm⁻³ using NaClO₄. The temperature of the solution and its pH were both maintained at 25 ± 0.1°C and 7.0 ± 0.1, respectively.

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