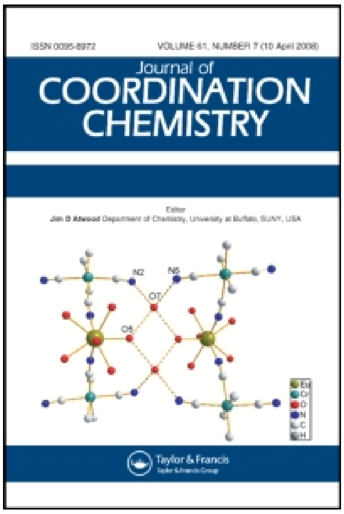

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Fornaro, Adalgiza and Coichev, Nina(1999) 'IRON(III) COMPLEX-CATALYZED REDUCTION OF TRIS(OXALATO)COBALTATE(III) BY L-ASCORBIC ACID', Journal of Coordination Chemistry, 46: 4, 519 — 532
To link to this Article: DOI: 10.1080/00958979908054916
URL: http://dx.doi.org/10.1080/00958979908054916

J. Coord. Chem., 1999, Vol. 46, pp. 519–532
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IRON(III) COMPLEX-CATALYZED REDUCTION OF TRIS(OXALATO)COBALTATE(III) BY L-ASCORBIC ACID

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(Received 28 January 1997; Revised 16 October 1997; In final form 6 April 1998)

Kinetic studies of the reduction of tris(oxalato)cobaltate(III) by L-ascorbic acid (H_2A) were investigated as a function of pH, buffer composition, iron(III) ion concentration and for different iron(III) complexes (EDTA, Cl^-, bipy and phen). The redox process was followed at 600 nm, (25.0 ± 0.1)°C, under *pseudo*-first-order conditions: $[H_2A] = 3.00 \times 10^{-2}$ M and $[Co(C_2O_4)_3^{3-}] = 3.00 \times 10^{-3}$ M in the presence of $[EDTA] = 3.15 \times 10^{-3}$ M and ionic strength 1.0 M (NaCl). A strong pH dependence shows reactivity $H_2A < HA^- < A^{2-}$. The Fe(III)/EDTA complex catalyzes the reaction with HA^- but not with A^{2-} or H_2A, showing a maximum catalytic effect around pH 7.5. The *pseudo*-first-order rate constant is proportional to iron(III) concentration in the range of $(0.2\text{–}10.0) \times 10^{-5}$ M. EDTA has a significant effect on the catalytic ability of the iron(III) ion while bipyridine and phenanthroline completely inhibit its activity. The order of catalytic activities is in agreement with the variation in reduction potential of the iron(III) complexes for the different ligands. When Cu(II) is used as a catalyst, EDTA completely inhibits its catalytic effect; in the presence of Cl^-, Cu(II) is a better catalyst than Fe(III).

Keywords: Ascorbic acid; iron(III); tris(oxalato)cobaltate(III); catalysis; kinetic studies

INTRODUCTION

The oxidation reactions of L-ascorbic acid (H_2A) are of fundamental interest in biochemistry, electrochemistry, pharmacology and other fields, since it is a strong reducing agent in aqueous solution.[1–3]

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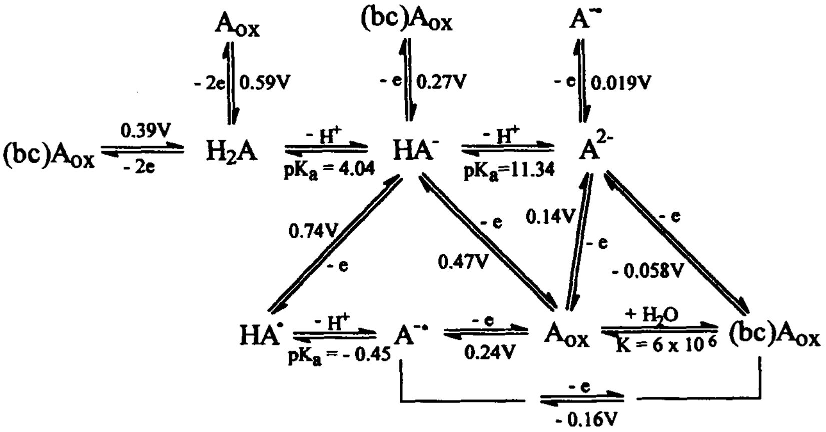
Ascorbic acid has two acidic protons (p$K_a = 4.04$ and 11.34). The acid–base and redox properties, based on the literature data,[1,4] involving the species H_2A, HA^-, A^{2-}, the radicals $HA^{\bullet}$ and $A^{-\bullet}$, and the L-dehydro ascorbic acid (A_{OX}) are summarized in Scheme 1. Also included are the hydration and cyclization of A_{OX} with formation of the bicyclic L-dehydro form, (bc)A_{OX}.



SCHEME 1 Reduction potentials *vs.* SHE and acidity constants for ascorbic acid and related species, at 25°C and ionic strength 0.2 M.[1,4]

Studies on the oxidation reactions of L-ascorbic acid by different metal ion complexes, have proposed formation of the protonated ascorbate free radical, ($H_2A^{+\bullet}$ or $HA^{\bullet}$) but not ($A^{-\bullet}$) in the rate-determining step.[3–9]

Oxidation of L-ascorbic acid by $[Co(C_2O_4)_3]^{3-}$ was studied in basic ($8 < pH < 10$)[8] and acidic ($3.2 < pH < 4.7$)[9] solution. The reaction in acid results in formation of L-dehydroascorbic acid (A_{OX}) according to the overall reaction **1**.

$$H_2A + 2[Co(C_2O_4)_3]^{3-} \longrightarrow A_{OX} + 2H^+ + 2[Co(C_2O_4)_3]^{4-} \qquad \mathbf{1}$$

These studies indicate an outer-sphere electron-transfer reaction with no evidence for formation of a stable intermediate. The reaction rate is very dependent on pH. Oxidation of A^{2-} is much faster than HA^- and H_2A.[8,9]

Rate data for the reduction of several iron(III) complexes and $[Co(C_2O_4)_3]^{3-}$ by ascorbic acid are presented in Table I. The data show the strong influence of pH and the nature of the ligand. Iron(III) complexes react much faster than $[Co(C_2O_4)_3]^{3-}$, which may explain the catalytic effect of an iron(III) ion.

TABLE I Rate constant for a series of oxidation reactions of ascorbic acid

Redox partners	*Rate constant at* 25°C ($M^{-1}\,s^{-1}$)	*Reference*
$[Co(C_2O_4)_3]^{3-}/H_2A$	1.2×10^{-4}	[9]
$[Co(C_2O_4)_3]^{3-}/HA^-$	4.1×10^{-3}	[9]
$[Co(C_2O_4)_3]^{3-}/HA^-$	7.0×10^{-3}	Present work
$[Co(C_2O_4)_3]^{3-}/A^{2-}$	20	[8]
$[Co(C_2O_4)_3]^{3-}/A^{2-}$	10.8	Present work
$[Fe(phen)_3]^{3+}/H_2A$	2×10^5	[9]
$[Fe(phen)_3]^{3+}/HA^-$	6×10^8	[9]
$[Fe(H_2O)_6]^{3+}/H_2A$	3.4	[5]
$[Fe(H_2O)_5OH]^{2+}/H_2A$	1.7×10^3	[5]
$[Fe(III)/EDTA]/HA^-$	2.8×10^3	[10]
$[Fe(C_2O_4)_3]^{3-}/HA^-$	2.1×10^4	[6]
$(Fe(bipy)_2]^{3+}/H_2A$	8.2×10^{-2}	[11]
$[Fe(bipy)_3]^{3+}/HA^-$	5.4×10^8	[12]

Another item to consider is the reaction of Fe(II) with $[Co(C_2O_4)_3]^{3-}$, which was investigated by several authors.[13–15] When $[Co(C_2O_4)_3]^{3-}$ was kept at 5.0×10^{-2} M (about 30 fold excess over iron(II)) the k_{obs} value obtained for the redox reaction was $9.49\,s^{-1}$ and $k = 189.9\,M^{-1}\,s^{-1}$.[18]

Iron(III) catalysis of the oxidation of ascorbic acid by dissolved oxygen,[16,17] hydrogen peroxide[18] and peroxide-bound chromium[10] were reported.

In the present study the catalytic effect of iron(III) on the reduction of $[Co(C_2O_4)_3]^{3-}$ by L-ascorbic acid was investigated in the presence of several complexing agents, in different buffers and over a large range of pH. Previous work done by Ohashi *et al.* in 0.2 M perchloric acid, where the reaction is very slow, led to linear relationship of the initial rate of the reduction with the iron(III) concentration.[19] The present study provides an improved analytical method for iron(III) at pH = 7.8 ($HTris^+/Tris$) in the presence of EDTA.

EXPERIMENTAL

Materials

$K_3[Co(C_2O_4)_3]\cdot 3H_2O$ was prepared according to the method described by Booth.[20] L-ascorbic acid and all other chemicals were of analytical reagent grade (Merck or Aldrich) and used without further purification.

All solutions were prepared with deionized, distilled water obtained from a Nanopure system.

The iron(III) stock solution was prepared from Fe_2O_3 (99.999%) dissolved in hydrochloric acid. The Cu(II) stock solution was prepared from $CuSO_4\cdot 5H_2O$ and standardized with EDTA.

Several buffer solutions 0.4 M were prepared with: CH_3COOH/CH_3COO^- (pH 3.7, 4.4, 4.7 and 5.3); $H_2PO_4^-/HPO_4^{2-}$ (pH 6.3 and 6.9); tris(hydroxymethyl)aminomethane, $HTris^+/Tris$ (pH 7.4, 7.8 and 8.5); HCO_3^-/CO_3^{2-} (pH 9.2 and 9.6); citric acid/citrate, $H_2Cit^-/HCit^{2-}$ (pH 4.5 and 5.9). Universal buffer mixtures[21] consisting of phosphoric acid, acetic acid, boric acid (0.18 M each) and sodium hydroxide were used for pH in the range of 3.0–10.0. The ionic strength, 1.0 M, of the buffer solutions were adjusted with NaCl solution.

Working solutions were prepared by mixing 1 : 1 solutions of ascorbic acid and $[Co(C_2O_4)_3]^{3-}$ prepared immediately before use in a suitable buffer as follows:

A solution of L-ascorbic acid (6.00×10^{-2} M) was prepared with or without iron complexes of ethylenediaminetetraacetate (EDTA), chloride (Cl^-), 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen). Iron was introduced as iron(II), since it is rapidly reduced by the L-ascorbic acid.

The solution of 6.00×10^{-3} M $[Co(C_2O_4)_3]^{3-}$ was prepared in the presence or absence of 6.30×10^{-3} M EDTA.

Measurements

pH measurements were performed with a Metrohm 654 pH meter equipped with a Metrohm glass combined electrode.

Spectrophotometric measurements were performed on a Hewlett Packard HP 8452A (diode-array) spectrophotometer and thermostated at (25.0 ± 0.1)°C by HP 89090A peltier temperature control accessory. The redox process was followed at 600 nm where the $[Co(C_2O_4)_3]^{3-}$ complex has a molar absorptivity of $150 \pm 10\ M^{-1}\,cm^{-1}$, and where none of the other reactants or products absorb significantly. An excess of ascorbic acid was used in all cases to ensure *pseudo*-first-order conditions. The kinetic traces were recorded on an IBM compatible computer and analyzed with the OLIS KINFIT set of programs.[22] The reported rate constants are the mean values of at least three determinations and subject to an average error of less than 5%. Since the reaction rate was not affected by dissolved oxygen in solution, the kinetic runs were carried out in solutions without removing the dissolved air.

RESULTS AND DISCUSSION

The variation of $[Co(C_2O_4)_3]^{3-}$ concentration from reduction by L-ascorbic acid, in the presence or absence of iron(III) ion, showed *pseudo*-first-order behavior. The rate of reaction increased with iron(III) ion concentration.

pH Influence

Uncatalyzed Reaction

The catalytic effect of iron(III) ion and acidity are shown in Figure 1. The experiments were carried out over a large range of pH, in universal buffer solution with excess EDTA. EDTA was added to avoid hydrolysis of iron(III) and precipitation of Co(II) oxalate at higher pH (pH > 8). In the presence of EDTA and absence of catalyst (at pH ~ 9) the reduction of $[Co(C_2O_4)_3]^{3-}$ by ascorbic acid is comparable to the results obtained by Martinez *et al.* [8]

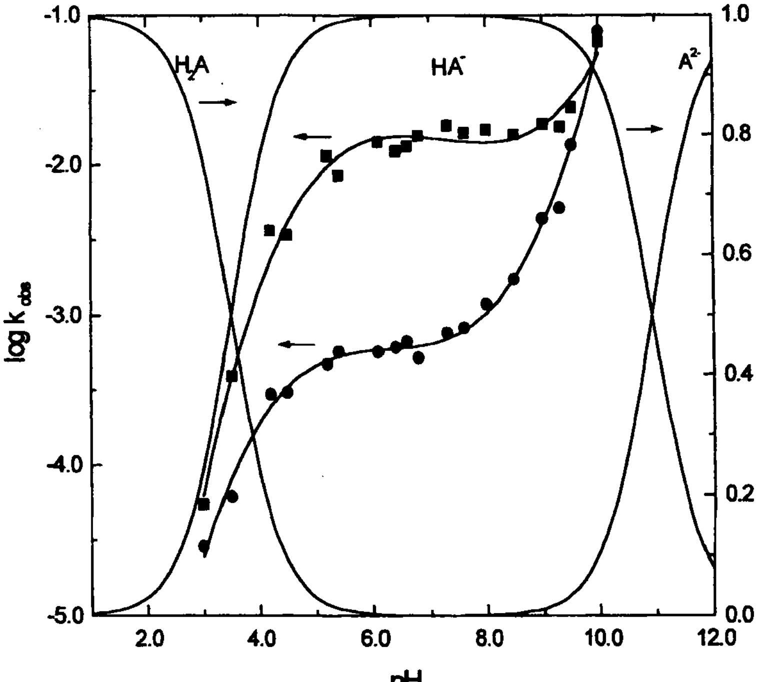


FIGURE 1 Distribution coefficient (α) of L-ascorbic acid, $K_1 = 3.2 \times 10^{-4}$ and $K_2 = 1.3 \times 10^{-11}$ M, as a function of pH. pH dependence of k_{obs} for the reduction of $[Co(C_2O_4)_3]^{3-}$ by L-ascorbic acid, without (●) and with [Fe(III)/EDTA] = 1.00×10^{-4} M (■). $[H_2A] = 3.00 \times 10^{-2}$ M; $[Co(C_2O_4)_3]^{3-} = 3.00 \times 10^{-3}$ M; [EDTA] = 3.15×10^{-3} M; ionic strength = 1.0 M (NaCl), (25.0 ± 0.1)°C in universal buffer mixtures.

The combination of kinetic data (log k_{obs} *vs.* pH) and the distribution diagram of ascorbic acid confirms the reactivity order $H_2A < HA^- < A^{2-}$ (Figure 1), as shown in the literature and expected by redox potentials (Scheme 1).[1,4] That is, at pH lower than 5, where H_2A and HA^- are present, the reaction is slower even in presence of iron(III). In the pH range 5–8, where HA^- species predominate, the k_{obs} is independent of the acidity. At pH 9–10 the reaction is much faster and the catalytic effect of iron(III) is negligible. At higher pH decomposition of A_{OX} becomes rapid, with the half-life for its decomposition decreasing from ~40 min at pH 6.7 to ~0.5 min at pH 8.6.[23]

No experiments at pH lower than 3 were carried out, due to the decomposition of the tris(oxalato)cobaltate(III)[24,25] and precipitation of H_4EDTA.[26] At this pH the catalytic effect of iron(III) is negligible.

The results presented in Figure 1 are in agreement with the following sequence of reactions:[8,9]

$$H_2A \rightleftharpoons HA^- + H^+ \qquad K_1 \qquad 2$$

$$HA^- \rightleftharpoons A^{2-} + H^+ \qquad K_2 \qquad 3$$

$$H_2A + [Co(C_2O_4)_3]^{3-} \longrightarrow H_2A^{+\bullet} + Co^{2+} + 3C_2O_4^{2-} \qquad k_a \qquad 4$$

$$HA^- + [Co(C_2O_4)_3]^{3-} \longrightarrow HA^{\bullet} + Co^{2+} + 3C_2O_4^{2-} \qquad k_b \qquad 5$$

$$A^{2-} + [Co(C_2O_4)_3]^{3-} \longrightarrow A^{-\bullet} + [Co(C_2O_4)_3]^{4-} \qquad k_c \qquad 6$$

$$H_2A^{+\bullet}/HA^{\bullet}/A^{-\bullet} + [Co(C_2O_4)_3]^{3-} \longrightarrow A_{OX} + [Co(C_2O_4)_3]^{4-} + 2H^+ \qquad \text{fast} \qquad 7$$

The rate of disappearance of $[Co(C_2O_4)_3]^{3-}$ is given by the rate law in equation **8**.

$$\frac{d\left[Co(C_2O_4)_3^{3-}\right]}{dt} = 2\left\{k_a[H_2A] + k_b[HA^-] + k_c\left[A^{2-}\right]\right\}\left[Co(C_2O_4)_3^{3-}\right]. \qquad 8$$

For the experimental data at $3 < pH < 6$ the rate law under *pseudo*-first-order conditions is given in **9**,

$$\frac{d\left[Co(C_2O_4)_3^{3-}\right]}{dt} = 2\left\{\frac{k_a[H^+] + k_bK_1}{[H^+] + K_1}\right\}[H_2A]_t\left[Co(C_2O_4)_3^{3-}\right] \qquad 9$$

which results in the expression for k_{obs} given in **10**, where $[H_2A]_t$ is the total ascorbic acid concentration.

$$k_{obs} = \frac{2k_a[H^+] + 2k_bK_1}{[H^+] + K_1}[H_2A]_t. \qquad \mathbf{10}$$

Under limiting conditions ($k_a \ll k_b$), this expression can be written as equation **11**.

$$\frac{1}{k_{obs}} = \frac{[H^+]}{2k_bK_1[H_2A]_t} + \frac{1}{2k_b[H_2A]_t}. \qquad \mathbf{11}$$

According to equation **11** a plot of k_{obs}^{-1} *vs.* $[H^+]$, for $3 < pH < 6$, is linear. From the slope and intercept $k_b = 7.0 \times 10^{-3}\,M^{-1}\,s^{-1}$ and $K_1 = 0.71 \times 10^{-4}\,M$, respectively. These values are of the same order as those of the literature $k_b = 4.1 \times 10^{-3}\,M^{-1}\,s^{-1}$.[9] By pH titration $K_1 = 1.12 \times 10^{-4}\,M$ at 1.0 M ionic strength and 25°C.[9]

For the experimental data at $8.5 < pH < 10$ the rate law is described by the equations:

$$\frac{d\left[Co(C_2O_4)_3^{3-}\right]}{dt} = 2k_c\left[A^{2-}\right]\left[Co(C_2O_4)_3^{3-}\right] = 2k_c\frac{K_2[H_2A]_t}{[H^+]}\left[Co(C_2O_4)_3^{3-}\right] \qquad \mathbf{12}$$

and

$$k_{obs} = 2k_c\frac{K_2[H_2A]_t}{[H^+]}. \qquad \mathbf{13}$$

Considering $K_2 = 1.26 \times 10^{-11}\,M$,[8] the $k_c = 10.8\,M^{-1}s^{-1}$ was obtained from the slope of the plot of k_{obs} *vs.* $[H^+]^{-1}$. The literature value is $k_c = 20\,M^{-1}\,s^{-1}$, in universal buffer mixtures and the ionic strength adjusted with $NaClO_4$.[8]

Catalyzed Reaction

The results from different pH and buffer media are presented in Figure 2. The k_{obs} values depend linearly on the iron(III) concentration according to equation **14**,

$$k_{obs} = k_{spe}[Fe(III)] + k_{unc} \qquad \mathbf{14}$$

where the intercept (k_{unc}) is k_{obs} for the uncatalyzed reaction and the slope (k_{spe}) is the specific rate constant ($M^{-1}\,s^{-1}$) for the iron(III) catalyzed reaction.

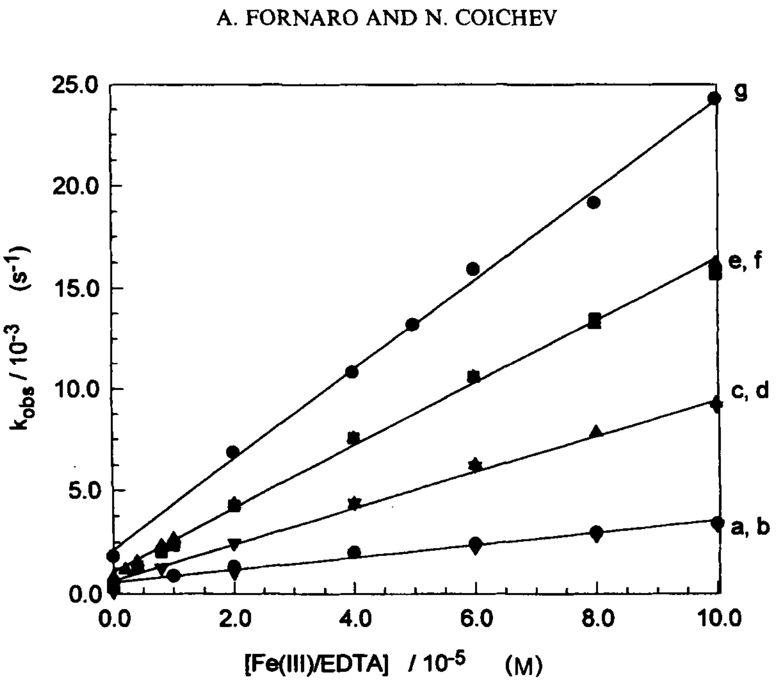


FIGURE 2 Influence of pH, buffer and iron(III) ion concentration on the k_{obs} values. $[H_2A] = 3.00 \times 10^{-2}$ M; $[Co(C_2O_4)_3]^{3-} = 3.00 \times 10^{-3}$ M; $[EDTA] = 3.15 \times 10^{-3}$ M; ionic strength = 1.0 M (NaCl), (25.0 ± 0.1)°C. Buffers: universal buffer pH (a) 4.5, (e) 6.8 and (f) 7.6; CH_3COOH/CH_3COO^- (b) pH 4.5; $H_2Cit^-/HCit^{2-}$ (c) pH 5.9; $H_2PO_4^-/HPO_4^{2-}$ (d) pH 6.9; $HTris^+/Tris$ (g) pH 7.8.

The Fe(III)/EDTA complex catalyzes the reaction with HA^- but not with A^{2-} or H_2A, and the curves, in Figure 1, are coincident at pH 9–10 and pH < 3.

Figure 3 shows the difference of the k_{obs} values (taken from Figure 1) of the catalyzed and uncatalyzed reaction as a function of pH, which maximizes at pH 7.5 where $[H_2A]_t = [HA^-]$. This is also observed from the dependence of k_{spe} *vs*. pH.

The characteristic pH dependence found in Figure 3 can be related to the acid–base equilibria of Fe(III)/EDTA in aqueous solutions. The Fe(III)/EDTA complex, seven coordinate with one coordination site occupied by a very labile water molecule, will account for the efficient formation of the inner-sphere complex in equation **16**. It was reported that $[Fe(EDTA)(H_2O)]^-$, exhibits one deprotonation step in the range pH 4–11, which is assigned to reaction **15**. The value of pK_{a1} varied between 7.2 and 7.8 depending on the experimental conditions employed, especially the ionic strength of the medium. On increasing the pH, deprotonation of the

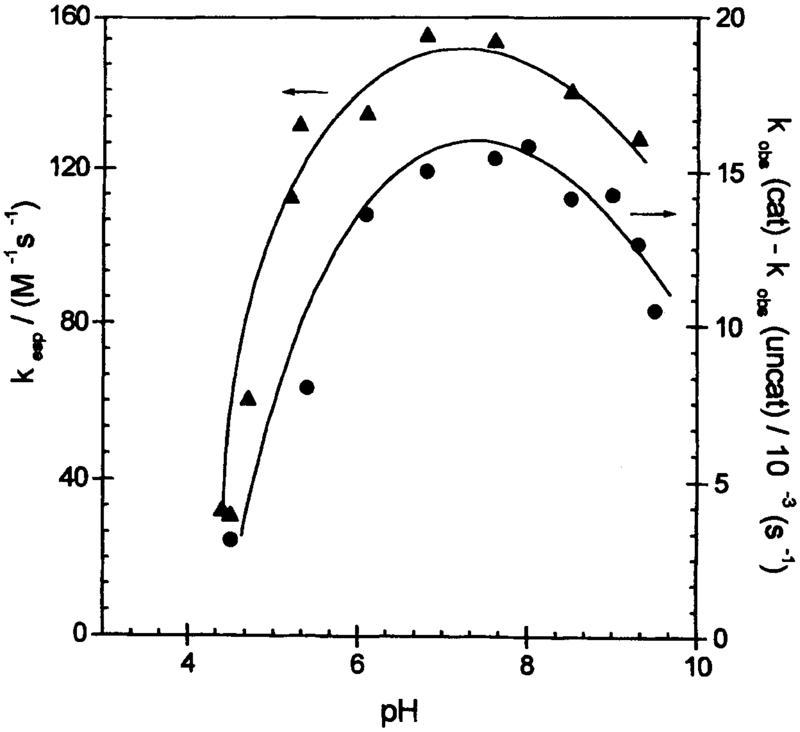


FIGURE 3 Difference between k_{obs} values for the catalyzed and uncatalyzed reactions (from Figure 1) and k_{spe} as a function of pH in universal buffer.

coordinated water molecule produces a hydroxo monomer, that is substitution inert, and accounts for the decrease in catalytic activity at $pH > 8$.[27]

$$[Fe(EDTA)(H_2O)]^- \rightleftharpoons [Fe(EDTA)(OH)]^{2-} + H^+ \quad K_{a1} \qquad 15$$

The weakly associated complex between Fe(III)/EDTA and ascorbate (equation 16) must be considered. Formation of this complex is followed by a redox reaction with ascorbic acid which results in the destruction of the complex. The reaction rate is governed by generation of the radical $HA^\bullet$.[10]

In the presence of iron(III) as a catalyst and in the presence of EDTA the mechanism can be described by the sequence of reactions:

$$Fe(III)(EDTA) + HA^- \rightleftharpoons Fe(III)(EDTA)(HA^-) \qquad 16$$

$$Fe(III)(EDTA)(HA^-) \longrightarrow Fe(II)(EDTA) + HA^\bullet \qquad 17$$

$$Fe(II)EDTA + [Co(C_2O_4)_3]^{3-} \longrightarrow Fe(III)EDTA + Co^{2+} + 3C_2O_4^{2-} \qquad 18$$

$$HA^\bullet + [Co(C_2O_4)_3]^{3-} \longrightarrow A_{OX} + Co^{2+} + 3C_2O_4^{2-} \qquad \textbf{19}$$

$$Fe(III)EDTA + HA^\bullet \longrightarrow Fe(II)EDTA + A_{OX} + H^+ \qquad \textbf{20}$$

In the reaction sequence (**16–20**), the electron transfer reaction between Co(III) and Fe(II) is much faster than the reaction of Co(III) complex with ascorbic acid, and the reaction of Fe(III) with ascorbic acid is even faster (Table I).

Effect of the Buffer Medium Composition Influence

There is a marked influence of the buffer composition on the k_{obs} value. For instance, according to the data in Figure 1, in the pH range of 5.5–8.0 the k_{obs} values are constant, while in Figure 2 the k_{obs} values vary with the buffer composition.

In $HTris^+/Tris$ the reaction is much faster and the $H_2PO_4^-/HPO_4^{2-}$ buffer has a inhibiting effect compared to universal buffer. In $H_2Cit^-/HCit^{2-}$ buffer ($pH = 5.9$) the results were similar to $H_2PO_4^-/HPO_4^{2-}$ ($pH = 6.9$) buffer. At $pH = 4.5$ the k_{obs} values obtained in CH_3COOH/CH_3COO^-, $H_2Cit^-/HCit^{2-}$(not shown in Figure 2) and universal buffer were the same. Higher k_{obs} values were obtained in $HTRIS^+/TRIS$ ($pH = 7.2–8.0$) buffer, where the HA^- predominates in solution.

When HCO_3^-/CO_3^{2-} buffer solutions ($pH = 9.2$ and 9.6) were used, a very fast decomposition of A_{OX} was observed with formation of brownish product.

The influence of the nature of the buffer, on the catalyzed reaction, can be explained because a wide variety of iron(III) complexes, including hydroxo complexes and other anions form according to the buffer and the pH used. Ogata and Kosugi explained the effect of additives on the rate in terms of "ligand effect" which includes coordination ability, *trans* effect and an instability effect of the anion.[28]

Ghosh and Gold[10] pointed out the presence of acetate complexes and hydroxo iron(III) species at pH 4.4. As shown in Table I, the nature of the ligand has a large influence on the kinetics for reaction of iron(III) with ascorbic acid.

Hynes and Kelly[29] proposed formation of $[Fe(H_2O)_5Cl]^{2+}$ which reacts significantly faster than $[Fe(H_2O)_6]^{3+}$ with H_2A. As sodium chloride was used in our experiments to maintain the ionic strength a complex could be formed at low pH.

Influence of Iron(III) Complex

The catalytic effect of iron(III) present as complexes, with EDTA, phen, bipy and Cl^- was investigated. A series of experiments presented in Figure 2 show higher k_{obs} values at pH 7.5; additional experiments were carried out on $HTris^+/Tris$ buffer.

As shown in Figure 4, EDTA has a significant effect on iron(III) as a catalyst, while bipy and phen completely inhibit its activity. This order of catalyst activities, depending on the attached ligand, is in agreement with the reduction potential for the complexes. The data in Table II show that the order of reducing power of the different iron(III) complexes is: EDTA < chloride < bipyridine = phenanthroline.

Although Fe(II)/EDTA is extremely oxygen sensitive and easily oxidized to Fe(III)/EDTA, experiments carried out in the presence and absence of

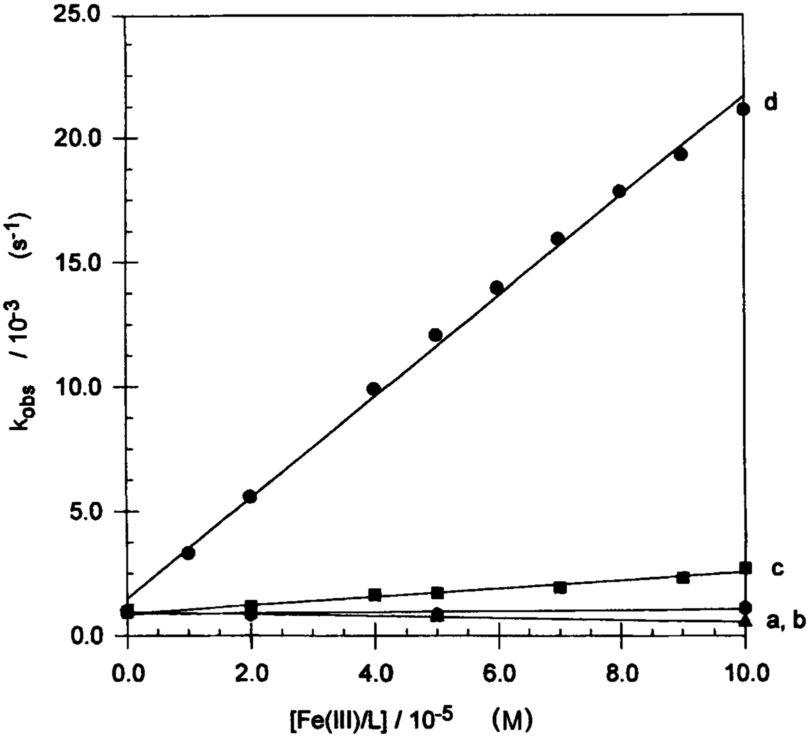


FIGURE 4 k_{obs} as a function of iron(III) complex concentration in $HTris^+/Tris$ buffer (pH 7.2) and absence of excess EDTA. $[H_2A] = 3.00 \times 10^{-2}$ M; $[Co(C_2O_4)_3]^{3-} = 3.00 \times 10^{-3}$ M; ionic strength = 1.0 M (NaCl), (25.0 ± 0.1)°C. L = (a) bipy, (b) phen, (c) Cl^- and (d) EDTA.

TABLE II Formal reduction potentials *vs.* SHE for different complexes of Fe(III)/Fe(II) and Co(III)/Co(II)[29,30]

Redox partners	*E* (Volts)
$Fe(phen)_3^{3+} + e^- \rightleftharpoons Fe(phen)_3^{2+}$	1.12
$Fe(bipy)_3^{3+} + e^- \rightleftharpoons Fe(bipy)_3^{2+}$	1.096
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$ (HCl)	0.77
$Fe(EDTA)^- + e^- \rightleftharpoons Fe(EDTA)^{2-}$	0.12
$[Co(C_2O_4)_3]^{3-} + e^- \rightleftharpoons [Co(C_2O_4)_3]^{4-}$	0.57

TABLE III k_{obs} values as a function of the concentration of iron(III) or copper(II) complexes, [M/L]. $[H_2A] = 3.00 \times 10^{-2}$ M; $[Co(C_2O_4)_3]^{3-} = 3.00 \times 10^{-3}$ M; ionic strength = 1.0 M (NaCl), (25.0 ± 0.1)°C and $HTris^+$/Tris buffer (pH 7.2).

$[M/L]/10^{-5}$ M	$k_{obs}/10^{-3}\,s^{-1}$			
	$Cu(II)/Cl^-$	$Fe(III)/Cl^-$	Cu(II)/EDTA*	Fe(III)/EDTA*
0	0.95	0.95	0.53	0.53
1.0	1.4	0.99	0.53	3.2
2.0	1.9	1.2	0.54	5.6
5.0	3.3	1.8	0.52	13.5
10.0	5.4	2.7	0.53	22.3

*$[EDTA] = 3.15 \times 10^{-3}$ M.

oxygen had the same values of the rate constants, since H_2A was kept in large excess.

The effect of Fe(III)/Fe(II) redox potential (Table II) is on regeneration of the Fe(III) catalyst according to equation **18**. The relative values of the reduction potential for different Fe(III)/Fe(II) complexes and $[Co(C_2O_4)_3]^{3-}/[Co(C_2O_4)_3]^{4-}$ show that only with $[Fe(EDTA)]^{2-}$ is the redox reaction indicated by equation **18** thermodynamically favored.

We did similar experiments on the reduction of $[Co(C_2O_4)_3]^{3-}$ by H_2A using Cu(II) instead of Fe(III) at pH = 7.2. Cu(II) has bigger effect than Fe(III) with chloride ligands, and, in contrast to Fe(III), EDTA completely inhibits catalytic activity of Cu(II) (Table III). The present results with Cu(II) cannot be compared with the Davies studies[32] which were done at pH = 2.5 in perchlorate medium with the Cu^{2+} ion kept in 10 fold excess over $[Co(C_2O_4)_3]^{3-}$.

The Cu(II) ion has been investigated as a catalyst for the oxidation of ascorbic acid by molecular oxygen.[13,14,28,33-36] In several studies by Taqui Khan and Martell the rate of this reaction is much faster catalyzed by iron(III) chelates than by Cu(II) chelates.[16,17] They proposed a pre-equilibrium with complex formation similar to that described by the equations **16** and **17**.

The reaction of L-ascorbic acid with oxygen and other oxidizing agents is catalyzed by transition metal ions;[1–3] sometimes solutions are stabilized by the addition of EDTA, which complexes the metal ions and arrests the catalysis. The present studies, show that for iron(III) EDTA increases its catalytic activity.

Acknowledgments

The authors gratefully acknowledge financial support from Brazilian agencies: FAPESP (Fundação de Amparo á Pesquisa do Estado de São Paulo) and CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico).

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