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Kinetics and Mechanism of the Oxidation of Ascorbic Acid by Tris(1,10-phenanthroline)iron(III) and Its Derivatives in Aqueous Acidic Perchlorate Media

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The kinetics of the oxidation of ascorbic acid (H_2A) by various substituted iron(III) 1,10-phenanthroline complexes ($Fe^{III}L_3$) have been investigated at 6.0, 20.0, and 35.0 °C in the range of perchloric acid concentration from 0.30 to 1.00 M. The experimental results agree with the rate law $-d[Fe^{III}L_3]/dt = k[Fe^{III}L_3][H_2A][H^+]^{-1}$. The differences in the oxidation rates for different complexes have been disucssed in terms of change of free energies of reaction, with the aid of the Marcus theory.

Introduction

The kinetics and mechanism of oxidation of ascorbic acid (H_2A) to dehydroascorbic acid (A) with different oxidizing agents have been investigated.[1] Particular interest has been devoted to metal ion catalyzed oxidation by molecular oxygen,[2] and, among the different metal ions, Fe(III) complexes have received large attention. Thus the reactions of ascorbic acid with iron(III) perchlorate,[3] hexacyanoferrate(III),[4] and iron(III) aminopolycarboxylic acid complexes[5] have been elucidated.

The present paper attempts to clarify the mechanism of oxidation of ascorbic acid with tris(1,10-phenanthroline)iron(III) and its derivatives (later referred to as $Fe^{III}L_3$) in aqueous acidic perchlorate media, in order to obtain additional information about the thermodynamic and reactivity parameters of ascorbic acid.

Experimental Section

Reagents. 1,10-Phenanthroline and its derivatives were supplied by K&K. Ascorbic acid was purchased from Merck. $Fe^{II}L_3$ were obtained as previously reported.[6] $Fe^{III}L_3$ were prepared by oxidation of the corresponding $Fe^{II}L_3$ in sulfuric acid solution by lead dioxide and precipitated as perchlorate salts. The following abbreviations were adopted for the different complexes: $Fe^{III}nphen_3$ for tris(5-nitro-1,0-phenanthroline)iron(III); $Fe^{III}cphen_3$ for tris(5-chloro-1,10-phenanthroline)iron(III); $Fe^{III}phen_3$ for tris(1,10-phenanthroline)iron(III); $Fe^{III}mphen_3$ for tris(5-methyl-1,10-phenanthroline)iron(III); $Fe^{III}dmphen_3$ for tris(5,6-dimethyl-1,10-phenanthroline)iron(III). Perchloric acid and sodium perchlorate, purchased from Merck and C. Erba, respectively, were used to bring the solutions to proper acidity and ionic strength. Solutions of ascorbic acid and of $Fe^{III}L_3$ were prepared immediately before use. Twice distilled water was used.

Kinetic Measurements. The experiments were carried out with a Durrum-Gibson stopped-flow spectrophotometer by following the reaction progress at the absorption maximum of $Fe^{II}L_3$. The runs were carried out at 6.0, 20.0, and 35.0 °C. The observed rate constants were evaluated by treating the points of a single run with a weighted least-squares method. In the estimation of other kinetic parameters, weights were assigned based on the standard deviation of the single kinetic runs (4–6%).

Potentiometric Measurements. The first dissociation constant of ascorbic acid was determined by potentiometric titration at 6.0, 20.0, and 35.0 °C, at μ = 1.0 M, with a Metrohm E388 potentiometer equipped with glass and calomel electrodes. The pH meter was calibrated with acetate buffers as well as with standard $HClO_4$. The concentration of hydrogen ion has been calculated from the pH measurements; activity coefficients of the ions have been evaluated by means of Davies equation.[7] The solutions of ascorbic acid were prepared with air-free distilled water and purified nitrogen was bubbled through the cell during the titration.

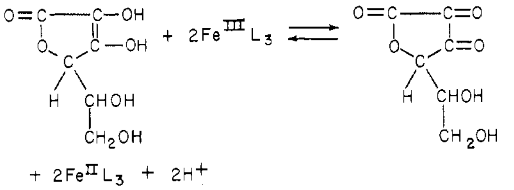
Results

Table I. Acidity Dependence of the Second-Order Rate Constants ($l.\ mol^{-1}\ s^{-1}$) for the Reaction of Ascorbic Acid with $Fe^{III}L_3$ at 20.0 °C and μ = 1.0 M[a]

Oxidant	$[HClO_4]$, mol $l.^{-1}$				
	0.30	0.40	0.50	0.70	1.00
Fe^{III}-nphen$_3$		4.7×10^6	4.5×10^6	4.4×10^6	4.2×10^6
Fe^{III}-cphen$_3$		1.85×10^6	1.45×10^6	1.1×10^6	8.0×10^5
Fe^{III}-phen$_3$		3.5×10^5	2.8×10^5	2.2×10^5	1.55×10^5
Fe^{III}-mphen$_3$	2.7×10^5	2.3×10^5	1.7×10^5	1.2×10^5	8.2×10^4
Fe^{III}-dmphen$_3$	1.65×10^5	1.35×10^5	9.5×10^4	7.4×10^4	5.2×10^4

[a] The concentration range investigated was $[Fe^{III}L_3] = 4\text{–}6 \times 10^{-6}$ and $[H_2A] = 5.0\text{–}30 \times 10^{-5}$ M; for the reactions with $Fe^{III}nphen_3$ and $Fe^{III}cphen_3$, second-order conditions were adopted: $[Fe^{III}L_3] = 4\text{–}6 \times 10^{-6}$ and $[H_2A] = 5\text{–}40 \times 10^{-6}$ M.

Stoichiometry. The absorbances at equilibrium (at the wavelengths of maximum absorption of $Fe^{II}L_3$) of reaction mixtures containing $[H_2A] = 1.0 \times 10^{-5}$ M and $Fe^{III}L_3$ at different concentrations were recorded in order to estimate the stoichiometric ratio. The data showed that the reactions may be represented by the following stoichiometric equation:



(1)

Dissociation Constants. The first dissociation constant of ascorbic acid (K_1), obtained from titration curves, was found to be 6.6×10^{-5}, 9.3×10^{-5}, and 1.3×10^{-4} mol $l.^{-1}$ at 6.0, 20.0, and 35.0 °C, respectively (μ = 1.0 M, $NaClO_4$). These values can be compared with 3.24×10^{-5} (0.4 °C) and 9.16×10^{-5} (25.0 °C) evaluated at μ = 0.10 M, KNO_3.[2]

Kinetics. When operating in pseudo-first-order conditions (that is with an excess of the organic substrate in respect to $Fe^{III}mphen_3$, $Fe^{III}phen_3$, and $Fe^{III}dmphen_3$), plots of ln ($A_\infty - A_t$) (where A_∞ and A_t represent the absorbance at equilibrium and at time t) as a function of time were linear up to 3 half-lives. The pseudo-first-order rate constants were also linearly dependent on the concentration of the reagent in excess (H_2A); moreover, an inverse dependence on acidity has been pointed out (see Table I and Figure 1), so that the following empirical rate law can be proposed

$$-{}^1/_2\, d[Fe^{III}L_3]/dt = k_0[Fe^{III}L_3][H_2A][H^+]^{-1} \qquad (2)$$

A different behavior has been observed when $Fe^{III}nphen_3$ is

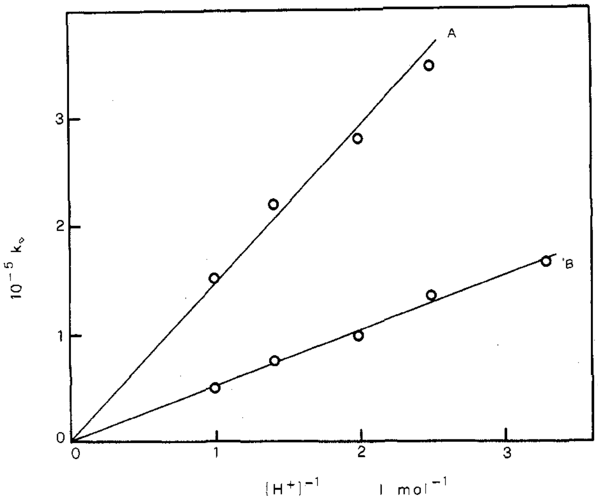


Figure 1. Acidity dependence of second-order rate constants (l. mol^{-1} s^{-1}, at 20.0 °C and $\mu = 1.0$ M) for the oxidation of ascorbic acid with: (A) $Fe^{III}phen_3$, and (B) $Fe^{III}dmphen_3$.

the oxidant: owing to the high rates of reactions, second-order conditions were adopted and, in the range 0.40–1.00 M of perchloric acid, an approximately constant value of the second-order rate constants was found.

Effect of $Fe^{II}L_3$. By following the runs at 360 nm (where $\epsilon_{Fe^{III}phen_3} = 5.5 \times 10^3$ and $\epsilon_{Fe^{II}phen_3} = 1.0 \times 10^3$ l. mol^{-1} cm^{-1}) the effect of an excess of $Fe^{II}phen_3$ on the reaction rate has been investigated. In the range of $Fe^{II}phen_3$ between 1 and 5×10^{-5} M, no appreciable effect has been observed.

Effect of Ionic Strength. In order to study the effect of ionic strength, kinetic runs (with $[H_2A] = 1 \times 10^{-5}$, $[Fe^{III}mphen_3] = 5 \times 10^{-6}$, $[HClO_4] = 0.10$ M and at 6.0 °C) were performed with increasing addition of $NaClO_4$ up to 0.40 M. The rate decreased with increasing ionic strength and a plot of log k_{obsd} as a function of $\mu^{1/2}/(1 + \mu^{1/2})$ exhibited a slope ca. −3, thus confirming that the reaction takes place through the interaction of a +3 and −1 charged species.

Discussion

$Fe^{III}L_3$ are well-known one-electron oxidants[6] and the oxidation of ascorbic acid has been shown to take place through the formation of an intermediate radical, further oxidized to dehydroascorbic acid.[1-5] Taking into account these considerations and the dependence on acidity as well as the ionic strength effect, the following sequence can be proposed:

$$H_2A \underset{}{\overset{\text{fast}}{\rightleftharpoons}} HA^- + H^+ \qquad (K_1) \tag{3}$$

$$Fe^{III}L_3 + HA^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Fe^{II}L_3 + HA\cdot \tag{4}$$

$$Fe^{III}L_3 + HA\cdot \xrightarrow{k_3} Fe^{II}L_3 + A + H^+ \tag{5}$$

This leads, by assuming a stationary steady state condition for HA·, to the following rate law

$$\frac{-[Fe^{III}L_3]'}{dt} = \frac{2k_2k_3K_1[Fe^{III}L_3]^2[H_2A][H^+]^{-1}}{k_{-2}[Fe^{II}L_3] + k_3[Fe^{III}L_3]} \tag{6}$$

which reduces to eq 2 if $k_3[Fe^{III}L_3] \gg k_{-2}[Fe^{II}L_3]$, as supported by the absence of the $Fe^{II}L_3$ effect, and then $k_0 = k_2K_1$ (in the experimental conditions ascorbic acid is essentially in H_2A form). Then the specific rate constants, k_2, can be evaluated at different temperatures for the investigated $Fe^{III}L_3$ (see Table II). It is noteworthy that the estimated second-order rate constants for the reaction of H_2A with $Fe^{III}nphen_3$ do not follow the acidity dependence of eq 2; then other contributions should be considered as rate determining, like precursor complex formation or the achievement of the diffusion-controlled limit.[8] Also kinetic measurements performed at higher acidities (at $\mu = 4.0$ M, with $LiClO_4$ or $NaClO_4$ as supporting electrolyte) did not give additional information; in fact the dependence upon $[H^+]$ observed when $NaClO_4$ is present is probably due to a medium effect (see Table III).[9]

Table II. Specific Rate Constants k_2 (l. mol^{-1} s^{-1}) for the Oxidation of Ascorbic Acid with $Fe^{III}L_3$ (20.0 °C and $\mu = 1.0$ M)

Oxidant	$E^{0\,a}$	k_2	$\Delta H^{\ddagger b}$	$\Delta S^{\ddagger c}$	$k_{calcd}{}^d$	Ref
Fe^{III}-nphen$_3$	1.25				2.6×10^{10}	This work
Fe^{III}-cphen$_3$	1.12	7.5×10^9	0.2	−12	5.8×10^9	This work
Fe^{III}-phen$_3$	1.06	1.5×10^9	1.2	−12	2.4×10^9	This work
Fe^{III}-mphen$_3$	1.02	7.9×10^8	2.1	−11	1.3×10^9	This work
Fe^{III}-dmphen$_3$	0.97	4.1×10^8	2.1	−12	5.3×10^8	This work
$Fe(CN)_6{}^{3-}$	0.68	8.6×10^2			8.0×10^2	4

[a] V, for oxidizing agent couples. [b] kcal mol^{-1}, the error is 0.7–1.0 kcal mol^{-1}. [c] cal deg^{-1} mol^{-1}, the error is 2.3–3.3 cal deg^{-1} mol^{-1}. [d] Calculated according to eq 8; $\Delta G^*{}_{Fe^{III}L_3/Fe^{II}L_3} = 3$ kcal mol^{-1}; $\Delta G^*{}_{Fe(CN)_6{}^{3-}/Fe(CN)_6{}^{4-}} = 11.4$ kcal mol^{-1} (this value has been adopted according to other Marcus theory applications;[15] recent observations[16] suggest a higher value for self-exchange rate (ca. 10^4); this leads to $k_{calcd} \simeq 5 \times 10^3$); $\Delta G^*{}_{HA\cdot/HA^-} = 4$ kcal mol^{-1} and $E^0{}_{HA\cdot/HA^-} = 0.93$ V.

Table III. Acidity Dependence of Second-Order Rate Constant for Reaction of Ascorbic Acid with $Fe^{III}nphen_3$ at 20.0 °C and $\mu = 4.0$ M[a]

$[HClO_4]$, mol l.$^{-1}$	$10^{-5} \times k$, l. mol^{-1} s^{-1}	
	$(NaClO_4)$	$(LiClO_4)$
1.00	3.3	2.1
1.50	3.0	2.1
2.00	2.7	1.9
3.00	2.2	1.8_5
4.00	1.7_5	1.7_5

[a] $[H_2A] = 2\text{-}5 \times 10^{-5}$, $[Fe^{III}nphen_3] = 4\text{-}5 \times 10^{-6}$ M.

The rate constants for the dissociation of $Fe^{III}L_3$ have been determined and are very low in respect to the presently observed reaction rates.[10] Hence the mechanism of electron transfer does not involve a prior dissociation of the ligand and a very likely mechanism is an electron transfer through an outer-sphere activated complex. When this mechanism is operating, a dependence of the reaction rate on the free energy change involved is expected and in fact a plot of log k_2 against E^0 (standard redox potentials of $Fe^{III}L_3/Fe^{II}L_3$ couples) is linear with slope ca. 8 (see Figure 2).

The Marcus theory[11] offers the possibility to correlate the free energies of electron-transfer reactions with the kinetic data and its applicability to redox reactions involving organic reversible systems has been verified in the case of quinols and catechols oxidized by hexachloroiridate(IV) and $Fe^{III}L_3$.[12]

ΔG^*, the free energies of activation, can be calculated from the rate constants, k, through eq 7 where Z is the collision

$$k = Z \exp(-\Delta G^*/RT) \tag{7}$$

number in solution (assumed 10^{11} l. mol^{-1} s^{-1}).

The free energy of activation is expressed in terms of reorientation parameter (assumed to be $2(\Delta G^*{}_{11} + \Delta G^*{}_{22})$, where $\Delta G^*{}_{11}$ and $\Delta G^*{}_{22}$ are the free energy of activation of the self-exchange reactions for the single reactant couples) and the free energy of reaction $\Delta G^{0\prime}$ ($\Delta G^{0\prime} = \Delta G^0 + w_p - w_r$, where ΔG^0 is the standard free energy of reaction for the prevailing

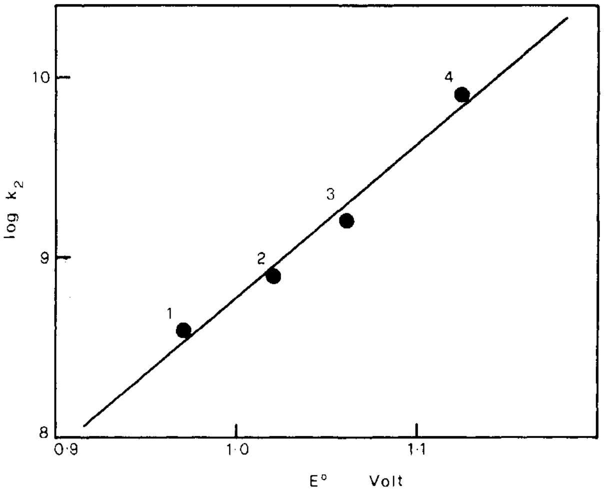


Figure 2. Relationship between the logarithms of the specific rate constants for the oxidation of ascorbic acid by different $Fe^{III}L_3$ (20.0 °C, $\mu = 1.0$ M) and the formal oxidation potentials of $Fe^{III}L_3/Fe^{II}L_3$ couples: (1) Fe^{III}dmphen$_3$; (2) Fe^{III}mphen$_3$; (3) Fe^{III}phen$_3$; (4) Fe^{III}cphen$_3$.

medium and temperature, and w_r and w_p are the coulombic work for bringing together reactants and products).

$$\Delta G^* = w_r + \lambda(1 + \Delta G^{\circ\prime}/\lambda)^2/4 \tag{8}$$

When both reactants are charged, the term w_r is given by

$$w_r = \frac{z_1 z_2 e^2}{D_s r^*} e^{-\kappa r^*} \tag{9}$$

where z_1 and z_2 are the charges of reactants, e the electron charge, D_s the static dielectric constant, and r^* the radius of the activated complex; the exponential coefficient is the Debye–Hückel term, where κ is the reciprocal Debye radius. It can be seen that at the present ionic strengths and with the investigated reagents the work terms are small.

The application of eq 8 to the present systems needs the knowledge of $\Delta G^*_{HA\cdot/HA^-}$ and $E^0_{HA\cdot/HA^-}$, coupled with $\Delta G^*_{Fe^{III}L_3/Fe^{II}L_3}$ and $E^0_{Fe^{III}L_3/Fe^{II}L_3}$. For $Fe^{III}L_3$, data concerning the oxidation potentials are available in the literature,[6] while for the intrinsic parameter both kinetic experiments and recent applications of Marcus theory suggest a value around 2.5–3.5 kcal mol^{-1}.[13] However, unfortunately no data are available for the parameters concerning ascorbic acid. The rate of electron exchange between HA^- and $HA\cdot$ should lie in the region 1×10^7–1×10^9 l. mol^{-1} s^{-1}, as observed for a series of reactions between radicals and parent molecules (see, for example, phenoxide ion with phenoxy radical[14] and the values previously derived for semiquinone/aromatic diol systems).[12]

Under these assumptions $\Delta G^*_{HA\cdot/HA^-}$ should be estimated to have a value ranging from 2.5 to 5.5 kcal mol^{-1} and tentatively ΔG^0 could be evaluated from the experimental ΔG^* of the reactions with $Fe^{III}L_3$ and $Fe(CN)_6{}^{3-}$ (another outer-sphere reaction whose intrinsic parameter is known).[15,16]

Thus the estimated $E^0_{HA\cdot/HA^-}$ should fall between 0.80 and 1.00 V. For example, the values of specific rate constants, calculated according to eq 8 with $\Delta G^*_{HA\cdot/HA^-} = 4$ kcal mol^{-1} and $E^0_{HA\cdot/HA^-} = 0.93$ V, are reported, together with the experimental ones in Table II.

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Registry No. Fe(III)nphen$_3$, 22327-24-8; Fe(III)cphen$_3$, 22327-23-7; Fe(III)phen$_3$, 13479-49-7; Fe(III)mphen$_3$, 15226-32-1; Fe(III)dmphen$_3$, 17378-72-2; ascorbic acid, 50-81-7.

References and Notes

(1) K. Kustin and D. L. Toppen, *Inorg. Chem.*, **12**, 1404 (1973); R. R. Grinstead, *J. Am. Chem. Soc.*, **82**, 3464 (1960); S. P. Mushran, M. C. Agrawal, R. M. Mehrotra, and R. Sanehi, *J. Chem. Soc., Dalton Trans.*, 1460 (1974); U. S. Mehrotra, M. C. Agrawal, and S. P. Mushran, *J. Inorg. Nucl. Chem.*, **32**, 2325 (1970).

(2) M. M. Taqui-Khan and A. E. Martell, *J. Am. Chem. Soc.*, **89**, 4179 (1967); **90**, 6011 (1968); **91**, 4668 (1969).

(3) G. S. Laurence and K. J. Ellis, *J. Chem. Soc., Dalton Trans.*, 1667 (1972).

(4) U. S. Mehrotra, M. C. Agrawal, and S. P. Mushran, *J. Phys. Chem.*, **73**, 1996 (1969).

(5) M. M. Taqui-Khan and A. E. Martell, *J. Am. Chem. Soc.*, **90**, 3386 (1968).

(6) M. H. Ford-Smith and N. Sutin, *J. Am. Chem. Soc.*, **83**, 1830 (1961).

(7) C. W. Davies, *J. Chem. Soc.*, 2093 (1938).

(8) S. Petrucci, "Ionic Interactions", Vol. II, Academic Press, New York, N.Y., 1971, Chapter 7.

(9) J. Holzwarth and L. Strohmaier, *Ber. Bunsenges. Phys. Chem.*, **77**, 1145 (1973); C. Lavallee and E. Deutsch, *Inorg. Chem.*, **11**, 3133 (1972).

(10) T. S. Lee, I. M. Kolthoff, and D. L. Leussing, *J. Am. Chem. Soc.*, **70**, 3596 (1948).

(11) R. A. Marcus, *J. Phys. Chem.*, **72**, 891 (1968), and references therein.

(12) E. Mentasti, E. Pelizzetti, and C. Baiocchi, *J. Chem. Soc., Dalton Trans.*, in press; E. Mentasti and E. Pelizzetti, *Int. J. Chem. Kinet.*, in press.

(13) M. W. Dietrich and A. C. Wahl, *J. Chem. Phys.*, **38**, 1591 (1963); I. Ruff and M. Zimonyi, *Electrochim Acta*, **18**, 515 (1973); E. Pelizzetti and E. Mentasti, *J. Chem. Soc., Dalton Trans.*, in press.

(14) D. Meisel, *Chem. Phys. Lett.*, **34**, 263 (1975).

(15) R. J. Campion, N. Purdie, and N. Sutin, *Inorg. Chem.*, **3**, 1091 (1964).

(16) R. J. Campion, C. F. Deck, P. King, Jr., and A. C. Wahl, *Inorg. Chem.*, **6**, 672 (1967).

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Magnetic Properties of $[(CH_3)_3NH]CoCl_3\cdot 2H_2O$ and Its Deuterium Analogue

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Measurements are reported of the specific heat and single-crystal principal susceptibilities in the helium region of $[(CH_3)_3ND]CoCl_3\cdot 2D_2O$ and compared with those of the protonic material. The effect of deuteration on the magnetic ordering temperature as well as on the exchange parameters is negligible. Because of the weak ferromagnetism of this material, sample size and shape affect the accuracy of magnetic measurements, causing a larger effect on the results than does the replacement of hydrogen by deuterium.

Introduction

A number of magnetic properties, as well as the synthesis and crystal structure, of orthorhombic $[(CH_3)_3NH]CoCl_3\cdot 2H_2O$ have been reported.[1-4] The material consists of chains of edge-sharing *trans*-$[CoCl_4(OH_2)_2]$ octahedra running parallel to the b axis; two chlorine atoms bridge the cobalt atoms. An additional chlorine atom in the lattice links the chains together by hydrogen bonding into a planar lattice with highly anisotropic magnetic behavior, and the trimethylammonium groups separate the planes both spatially and magnetically. With an antiferromagnetic T_c of 4.135 K, the zero-field magnetic susceptibilities and specific heat were