Kinetics and Mechanism of the Oxidation of L-Ascorbic Acid by Tris(oxalato)cobaltate(III) and Tris(1,10-phenanthroline)iron(III) Complexes in Aqueous Solution

By **Masaru Kimura*** and **Miwako Yamamoto** (née **Tsuruta**), Department of Chemistry, Faculty of Science, Nara Women's University, Nara 630, Japan
Shinichi Yamabe, Department of Chemistry, Nara University of Education, Nara 630, Japan

Kinetic studies of the oxidation of L-ascorbic acid by tris(oxalato)cobaltate(III), $[Co(C_2O_4)_3]^{3-}$, and tris(1,10-phenanthroline)iron(III), $[Fe(phen)_3]^{3+}$, have been made in an aqueous solution under varied conditions. The following mechanism of reaction is presented in accordance with the empirical results in solutions of pH 0.3—4.7: (i) $H_2A \overset{K_a}{\rightleftharpoons} HA^- + H^+$, (ii) $H_2A + X^n \xrightarrow{k_1} H_2A^{\cdot+} + X^{n-1}$, (iii) $HA^- + X^n \xrightarrow{k_2} HA^{\cdot} + X^{n-1}$, (iv) $X^n + H_2A^{\cdot+}$ (and $HA^{\cdot}$) $\xrightarrow{\text{rapid}} X^{n-1} + A + 2\,H^+$ (and H^+); where X = tris(oxalato)cobaltate(III) and tris(1,10-phenanthroline)iron(III) ions and $n = 3^-$ and 3+ respectively; H_2A and HA^- are the protonated species of the ascorbate ion. The rate constants k_1 and k_2, and the acid dissociation constant K_a were determined at 25 °C at ionic strength 0.1—1.0 mol dm^{-3}, and at an ionic strength of 1.0 mol dm^{-3} at five temperatures between 10 and 30 °C. The results obtained are discussed in terms of Marcus theory for the outer-sphere electron-transfer reaction. The energy of the highest occupied molecular orbital of the species H_2A and HA^-, and the differences in total electronic energy between $H_2A^{+\cdot}$ and H_2A, and between $HA^{\cdot}$ and HA^-, are calculated by using CNDO/2 MO, and they are presented for the comparison with the redox potentials estimated by applying the Marcus theory to the kinetic data.

L-ASCORBIC acid is well-known for its reducing properties in aqueous solution. The existence of the ascorbate free radicals in the one-electron oxidation of L-ascorbic acid has been confirmed by e.s.r. and kinetic measurements.[1] In the present paper, we make kinetic studies of the oxidation reactions of L-ascorbic acid with tris(oxalato)cobaltate(III) and with tris(1,10-phenanthroline)iron(III) in aqueous acidic solution, and present the most probable mechanisms of reaction. Recently,[2] we made a kinetic study of the oxidation of *o*-, *m*-, and *p*-benzenediols and estimated the standard redox potentials of each isomer by applying Marcus theory; [3] the redox potentials were found to correlate well with $E_{\text{h.o.m.o.}}$ and ΔE_T, respectively, the energies of the highest occupied molecular orbital and the difference in total electronic energies between radical molecule and the parent one, being theoretically calculated by using the CNDO/2 MO method.[4] In the present paper too, we have calculated $E_{\text{h.o.m.o.}}$ and ΔE_T for the protonated species H_2A and HA^- of L-ascorbic acid with the purpose of comparing the kinetic properties of these species; HA^- is much more easily oxidized than H_2A by both tris(oxalato)cobaltate(III) and tris(1,10-phenanthroline)iron(III) complex ions.

EXPERIMENTAL

Chemicals.—Reagent grade L-ascorbic acid from the Wako Pure Chemical Co. Inc. was used without further purification. The solutions of L-ascorbic acid were each prepared immediately before use. $K_3[Co(C_2O_4)_3]$ was synthesized by literature methods.[5,6] The solutions of $[Co(C_2O_4)_3]^{3-}$ were each prepared immediately before use. $[Fe(phen)_3][ClO_4]_3$ was prepared by oxidizing $[Fe(phen)_3]^{2+}$ with lead(IV) dioxide in dilute sulphuric acid solution; after removal of unchanged lead dioxide and lead(II) sulphate the perchlorate salt of tris(1,10-phenanthroline)iron(III) was precipitated by addition of $Na[ClO_4]$. The solid obtained was recrystallized from perchlorate solution. A stock solution of $[Fe(phen)_3]^{3+}$ was prepared by dissolving the perchlorate salt in concentrated perchloric acid (70%, v/v). The $[Fe(phen)_3]^{3+}$ is quite stable in perchloric acid and the concentration does not change for at least 3 months. Sodium perchlorate used for adjusting the ionic strength was recrystallized twice from aqueous solution. Deionized water was further distilled with addition of some permanganate in a glass still.

Kinetic Measurements.—The kinetic experiments were carried out with a Union RA-401 stopped-flow spectrophotometer for the reaction of L-ascorbic acid with $[Fe(phen)_3]^{3+}$ by following the increase of the absorbance of $[Fe(phen)_3]^{2+}$ at 510 nm, and with a Hitachi model 100-40 spectrophotometer for the reaction of L-ascorbic acid with $[Co(C_2O_4)_3]^{3-}$ by following the decrease of the absorbance of the cobalt(III) complex at 600 nm. The L-ascorbic acid concentrations were kept at least 10 times larger than the oxidizing agent concentrations in order to ensure pseudo-first-order conditions. The observed rate constants were evaluated by treating the points of a single run with a least-squares method for the reaction of L-ascorbic acid with $[Co(C_2O_4)_3]^{3-}$ and were evaluated by treating the kinetic curve of the average of 10 runs for the reaction of L-ascorbic acid with $[Fe(phen)_3]^{3+}$. The stopped-flow apparatus was equipped with a micro-computer system for memorizing and averaging the multiple runs. The acidity was kept constant in the range 0.11—0.5 mol dm^{-3} in perchloric acid for the reaction of L-ascorbic acid with $[Fe(phen)_3]^{3+}$, and the pH was kept constant in the range 3.2—4.7 by addition of NaOH or $HClO_4$ for the reaction of L-ascorbic acid with $[Co(C_2O_4)_3]^{3-}$; the pH was well buffered with excess ascorbic acid throughout the kinetic run. The pH of aliquot samples of the reaction solution was measured with a Hitachi–Horiba M-5 pH meter. Sodium chloride instead of potassium chloride was used for the electrolyte in the reference electrode in the pH meter. The ionic strength was adjusted by addition of $Na[ClO_4]$. The activity coefficients (f_i) at varied ionic strengths (I) were obtained by using $\log f_i = -0.358\, z_i^2 I^{\frac{1}{2}}/(1 + 10^8 a_i \cdot 0.2325\, I^{\frac{1}{2}})$ with $a_i = 9$ Å and $z_i = 1$.[7] The activity coefficients used were 0.88 (0.05), 0.85 (0.1), 0.83 (0.2), 0.79 (0.5), 0.78 (0.75), and 0.77 (1.0), with ionic strength (mol dm^{-3}) in parentheses.

RESULTS

Dissociation Constant of L-*Ascorbic Acid*.—The dissociation constants (K_a) for the reaction $H_2A \rightleftharpoons HA^- + H^+$ were determined by the pH titration of L-ascorbic acid at an ionic strength of 1.0 mol dm^{-3} at 10—30 °C, and at different ionic strengths at 25 °C. The values of K_a (mol dm^{-3}) determined are, at an ionic strength of 1.0 mol dm^{-3} with temperature (°C) in parentheses, 8.32×10^{-5} (10), 9.12×10^{-5} (15), 1.00×10^{-4} (20), 1.12×10^{-4} (25), 1.26×10^{-4} (30); and at 25 °C with ionic strength in parentheses, 1.10×10^{-4} (0.75), 1.05×10^{-4} (0.5), 1.00×10^{-4} (0.2), 9.55×10^{-5} (0.15), 8.32×10^{-5} (0.1), and 7.76×10^{-5} (0.05).

Stoicheiometry.—(a) *Reaction between* L-*ascorbic acid and tris*(*oxalato*)*cobaltate*(III). For the purpose of the examination of the stoicheiometry, the reaction was started at the initial concentration of 4.0×10^{-3} mol dm^{-3} for the each reactant at 25 °C. The aliquot samples were withdrawn at appropriate times and mixed with a solution of 0.05 mol dm^{-3} perchloric acid, 0.1 mol dm^{-3} sodium perchlorate, and 0.01% gelatin, where the concentrations are of those after the solution was mixed. Then the concentrations of L-ascorbic acid and/or $[Co(C_2O_4)_3]^{3-}$ were measured at 0.375 V *versus* s.c.e. (standard calomel electrode) and 0.150 V *versus* s.c.e. by using polarography. At 0.150 V *versus* s.c.e. only the reduction current of $[Co(C_2O_4)_3]^{3-}$ was measured, and at 0.375 V *versus* s.c.e. the total current due to the oxidation of L-ascorbic acid and the reduction of $[Co(C_2O_4)_3]^{3-}$ was measured. As a result, the mean of $[Co(C_2O_4)_3{}^{3-}]_{reacted}$/[L-ascorbic acid]$_{reacted}$ was 1.9 ± 0.2 for 10 reaction times.

TABLE 1

Second-order rate constants (k_0) for the reaction between L-ascorbic acid and tris(oxalato)cobaltate(III) [a]

Temp./°C	I/mol dm^{-3}	pH	10^3k_0/dm^3 mol^{-1} s^{-1}
15	1.0	3.52	0.734
		3.78	1.01
		3.95	1.30
		4.11	1.58
		4.32	2.06
		4.60	2.52
20	1.0	3.29	0.935
		3.50	1.34
		3.73	1.81
		3.94	2.35
		4.17	3.05
		4.54	3.94
25	1.0	3.27	1.42
		3.46	1.76
		3.62	2.40 [b]
		3.67	2.40
		3.87	3.20
		3.98	3.76 [b]
		4.02	3.94
		4.25	5.00
		4.48	5.94
		4.52	5.96 [b]
30	1.0	3.20	2.02
		3.43	2.88
		3.60	3.70
		3.81	4.58
		4.00	5.72
25	0.5	3.72	1.78
		3.79	1.97
		3.98	2.54
		4.11	2.88
		4.35	3.66
25	0.2	3.81	1.33
		4.19	2.06
		4.40	2.50
		4.67	3.13
25	0.1	3.68	0.851
		3.72	1.00, 13, [c] 127 [d]
		4.10	1.42
		4.25	1.64
		4.50	2.18

[a] Initial concentrations of L-ascorbic acid and $K_3[Co(C_2O_4)_3]$ are 0.1 and 0.003 mol dm^{-3} respectively. [b] As in *a*, but in the presence of 0.005 mol dm^{-3} ethylenediaminetetra-acetate. [c] As in *a*, but in the presence of 10^{-4} mol dm^{-3} copper(II) sulphate. [d] As in *a*, but in the presence of 5×10^{-4} mol dm^{-3} copper(II) sulphate.

(*b*) *Reaction between* L-*ascorbic acid and tris*(1,10-*phenanthroline*)*iron*(III). Since this reaction is very fast, the stoicheiometry can be determined by titrating L-ascorbic acid with $[Fe(phen)_3]^{3+}$, the concentration of the complex being measured as a monitor at 510 nm. The equivalent point showed that the L-ascorbic acid reacted with a two-fold amount of $[Fe(phen)_3]^{3+}$. Thus, the same stoicheiometry holds for both oxidants, and the stoicheiometric equations are described by (1) and (2) where A_T represents all the forms of L-ascorbic acid, and the other products are probably the dehydroascorbic acid and protons.

$$2[Co(C_2O_4)_3]^{3-} + A_T \longrightarrow 2\,Co^{II} + 6\,C_2O_4{}^{2-} + \text{other products} \quad (1)$$

$$2[Fe(phen)_3]^{3+} + A_T \longrightarrow 2\,[Fe(phen)_3]^{2+} + \text{other products} \quad (2)$$

Kinetics of Reaction.—(a) *Reaction between tris*(*oxalato*)-*cobaltate*(III) *and* L-*ascorbic acid*. The kinetic experiments for this reaction were carried out at pH 3.2—4.7 so that the thermal decomposition of $[Co(C_2O_4)_3]^{3-}$ would be negligible. When pseudo-first-order conditions are adopted, plots of $\ln A_t$ *versus* t were linear for at least half-life time; A_t indicates the absorbance of $[Co(C_2O_4)_3]^{3-}$ at 600 nm at a certain time (t) of reaction. Moreover, when second-order conditions were adopted, the second-order plots were also linear as long as pH was well buffered. The second-order rate constant (k_0) was determined under the various conditions and values are in Table 1. Plots of k_0 *versus* $K_a/([H^+] + K_a)$ showed straight lines with intercepts, under any conditions. Some examples for these plots are shown in Figure 1.

Thus, the rate law is described by equation (3) where $[A_T]$ indicates total concentration of all forms of L-ascorbic acid and can be set as $[A_T] = [H_2A] + [HA^-]$ under the present conditions of pH range.

$$-d[Co(C_2O_4)_3{}^{3-}]/dt = k_0[Co(C_2O_4)_3{}^{3-}][A_T] = 2\left\{k_1 + (k_2 - k_1)\frac{K_a}{[H^+] + K_a}\right\}[Co(C_2O_4)_3{}^{3-}][A_T] \quad (3)$$

Temperature dependence. According to the rate law of equation (3), the values of k_1 and k_2 were determined at 15—30 °C at an ionic strength of 1.0 mol dm^{-3} (Table 3). The activation parameters were calculated from Eyring's absolute rate expression [equation (4)] by assuming $\kappa = 1$, the results being tabulated in Table 4 together with other parameters.

$$k = \kappa\frac{kT}{h}\exp[\Delta S^{\ddagger}/R]\exp[-\Delta H^{\ddagger}/RT] \quad (4)$$

Effect of ionic strength. The rate of reaction (*i.e.*, k_0 and k_2) increased with increasing ionic strength, see Tables 1 and

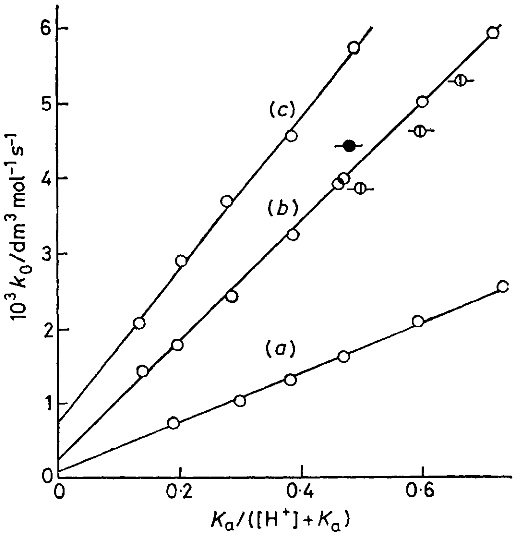

FIGURE 1 Examples of plots of k_0 *versus* $K_a/([H^+] + K_a)$. Initial concentrations of L-ascorbic acid were 0.1 mol dm^{-3} (○), 0.01 mol dm^{-3} (⦶), and 0.003 mol dm^{-3} (●); initial concentration of $[Co(C_2O_4)_3]^{3-}$ was 3.0 × 10^{-3} mol dm^{-3}; ionic strength = 1.0 mol dm^{-3}. Lines (*a*), (*b*), and (*c*) respresent the experiments at 15, 25, and 30 °C, respectively

3. Although the values of ionic strength employed in these experiments lie outside the Debye–Hückel region, the ionic strength dependence is as expected for the reactions between two ions of like charge sign.

Catalytic effect of copper(II) *ion.* The rate of reaction between L-ascorbic acid and $[Co(C_2O_4)_3]^{3-}$ was greatly accelerated by the presence of small amounts of copper(II) ion (refer to Table 1). The copper(II) ion catalysis was, however, remarkably reduced by the presence of the complex-forming agent, the oxalate ion; for example, although the initial rate was about 130 times faster in the presence of 5 × 10^{-4} mol dm^{-3} of copper(II) sulphate, it was reduced down to almost the same rate as in the absence of copper(II) by 0.01 mol dm^{-3} sodium oxalate being added before starting the reaction. The copper(II) catalysis is presumed to be due to the homogeneous cyclic reactions of Cu^{2+}/Cu^+, and thus the poisonous effect of the oxalate ion is presumed to be due to the complex formation of oxalato-complexes with the copper(II) ion which may be hardly reduced to copper(I) by L-ascorbic acid.

(*b*) *Reaction between tris*(1,10-*phenanthroline*)*iron*(III) *and* L-*ascorbic acid.* When pseudo-first-order conditions were adopted, plots of ln $(A_\infty - A_t)$ *versus* t were linear for 80% of a whole reaction, where A_∞ and A_t indicate the absorbance of $[Fe(phen)_3]^{2+}$ at infinite time and at time t of reaction, respectively. The observed first-order rate constants showed a first-order dependence on the L-ascorbic acid concentration. When second-order conditions were employed, the second-order plots were also linear, thus confirming the first-order dependence on each reactant. As seen in Table 2, the second-order rate constant (k_0) increased with decreasing acidity. Plots of k_0 *versus* $[H^+]^{-1}$ showed straight lines with intercepts; examples of these plots are given in Figure 2. Thus, the rate of reaction is described by equation (5).

$$-d[Fe(phen)_3{}^{3+}]/dt = k_0[Fe(phen)_3{}^{3+}][A_T] \\ = 2(k_1 + k_2K_a[H^+]^{-1})[Fe(phen)_3{}^{3+}][A_T] \quad (5)$$

TABLE 2

Second-order rate constants (k_0) for the reaction between L-ascorbic acid and tris(1,10-phenanthroline)iron(III) *

Temp./°C	I/mol dm^{-3}	[HClO$_4$]/ mol dm^{-3}	$10^{-6}k_0$/dm^3 mol^{-1} s^{-1}
10	1.0	0.50	0.355
		0.22	0.625
		0.14	0.835
		0.11	1.01
15	1.0	0.50	0.45, 0.48
		0.22	0.76, 0.70
		0.14	1.04
		0.11	1.17
20	1.0	0.50	0.520
		0.22	0.826
		0.17	1.00
		0.14	1.15
		0.11	1.44
25	1.0	0.50	0.62
		0.22	1.02
		0.14	1.37
		0.11	1.60, 1.71
30	1.0	0.50	0.734
		0.22	1.19
		0.17	1.45
		0.14	1.68
		0.11	2.03
25	0.75	0.50	0.787
		0.22	1.30
		0.17	1.69
		0.11	2.12
25	0.50	0.50	1.07
		0.22	1.86
		0.14	2.50
		0.11	2.98
25	0.25	0.25	2.81
		0.22	3.04
		0.17	3.69
		0.14	4.09
		0.11	4.54

* Initial concentrations of L-ascorbic acid and $[Fe(phen)_3]^{3+}$ are 1.0 × 10^{-4} and 5 × 10^{-6} mol dm^{-3} respectively.

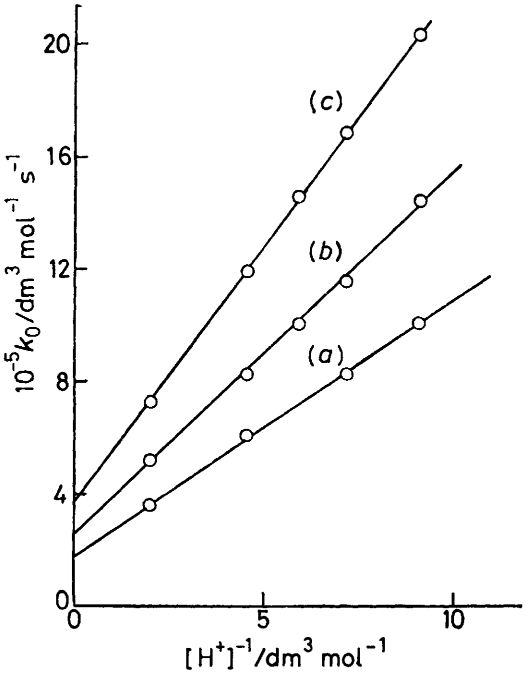

FIGURE 2 Examples of plots of k_0 *versus* $[H^+]^{-1}$. Conditions are those given in Table 2; ionic strength = 1.0 mol dm^{-3}. Lines (*a*), (*b*), and (*c*) represent the experiments at 10, 20, and 30 °C, respectively

TABLE 3

Temperature and ionic strength dependence of rate constants [a]

Temp./ °C	I/ mol dm^{-3}	$[Co(C_2O_4)_3]^{3-} + A_T$ [b]		$[Fe(phen)_3]^{3+} + A_T$ [c]	
		10^4k_1	10^3k_2	$10^{-5}k_1$	$10^{-8}k_2$
10	1.0	—	—	1.00 ± 0.04	5.29 ± 0.03
15	1.0	0.30 ± 0.03	1.69 ± 0.05	1.25 ± 0.05	5.81 ± 0.03
20	1.0	1.7 ± 0.08	2.68 ± 0.05	1.45 ± 0.05	6.15 ± 0.05
20	1.0	—	—	—	7.8 [d]
25	1.0	1.2 ± 0.1	4.06 ± 0.07	1.73 ± 0.06	6.45 ± 0.05
30	1.0	3.9 ± 0.2	5.4 ± 0.2	2.0 ± 0.1	7.02 ± 0.08
25	0.75	—	—	2.0 ± 0.1	9.0 ± 0.2
25	0.50	0.66 ± 0.14	2.75 ± 0.04	3.0 ± 0.1	12 ± 0.2
25	0.25	—	—	6.2 ± 0.2	19 ± 0.5
25	0.2	(−0.53)	1.9 ± 0.1	—	—
25	0.1	0.2 ± 0.6	1.5 ± 0.1	—	—

[a] In dm^3 mol^{-1} s^{-1}. [b] Conditions as in Table 1 and Figure 1. [c] Conditions as in Table 2 and Figure 2. [d] From Ref. 11.

TABLE 4

Parameters obtained for the reactions [a]

Reaction system	$\Delta H_{12}^{\ddagger}$/ kJ mol^{-1}	$\Delta S_{12}^{\ddagger}$/ J K^{-1} mol^{-1}	ΔG_{12}^{*}/ kJ mol^{-1}	$\Delta G_{12}^{\ominus}$/ kJ mol^{-1}	$E°(H_2A^{\cdot+}/H_2A)$/ V	$E°(HA^{\cdot}/HA^-)$/ V
$[Fe(phen)_3]^{3+}$–H_2A	21.3 ± 0.5	−73 ± 2	32.8 ± 0.2	18.7 ± 0.3	1.25, 1.27 [b]	
$[Fe(phen)_3]^{3+}$–HA^-	7.7 ± 0.3	−50 ± 1	12.4 ± 0.1	−23.2 ± 0.3		0.82, 0.85 [b]
$[Fe(phen)_3]^{3+}$–HA^-	8.8 ± 2 [c]	−46 ± 7 [c]	12.5 [c]			0.80, *ca.* 1.00 [c]
$[Co(C_2O_4)_3]^{3-}$–H_2A	108 ± 22	46 ± 61	84.3 ± 0.7	83.9 ± 0.7	1.44	
$[Co(C_2O_4)_3]^{3-}$–HA^-	54.3 ± 4.4	−109 ± 15	76.4 ± 0.5	75.2 ± 0.5		1.35

$E_{h.o.m.o.}(H_2A) = -0.425$ a.u.[d] $E_{h.o.m.o.}(HA^-) = -0.141$ a.u.[d] $\Delta E_T(H_2A^{+\cdot}/H_2A) = 0.389$ a.u.[d] $\Delta E_T(HA^{\cdot}/HA^-) = 0.082$ a.u.[d]

[a] The following parameters are used for the estimation of $E°$: $\lambda_{12} = 90$ and 97 kJ mol^{-1} for the reaction systems involving $[Fe(phen)_3]^{3+}$ and $[Co(C_2O_4)_3]^{3-}$ respectively; $E°\{[Fe(phen)_3]^{3+,2+}\} = 1.06$ V (N. Sutin and B. M. Gordon, *J. Am. Chem. Soc.*, 1961, **83**, 70); $E°\{[Co(C_2O_4)_3]^{3-,4-}\} = 0.57$ V (L. Hin-Fat and W. C. E. Higginson, *J. Chem. Soc. A*, 1967, 298). [b] These two values are estimated by using $\lambda_{12} = 86$ kJ mol^{-1} with $\Delta G_{11}^* = 23$ kJ mol^{-1} and $\Delta G_{22}^* = 20$ kJ mol^{-1} (refer to ref. 2). [c] From ref. 11. [d] The negatively large $E_{h.o.m.o.}$ and the larger ΔE_T correspond to the greater energy requirement for the oxidation. 1 a.u. = 2 626 kJ mol^{-1}.

Temperature dependence. The values of k_1 and k_2 defined in equation (5) were determined at 10—30 °C at an ionic strength 1.0 mol dm^{-3} (Table 3). The activation parameters were evaluated by assuming $\kappa = 1$ in equation (4) and are listed in Table 4 together with other parameters.

Effect of ionic strength. The rate of reaction decreased with increasing ionic strength (see Table 2), and both k_1 and k_2 decreased with increasing ionic strength. Although the ionic strengths lie outside the Debye–Hückel region, the ionic strength dependence is expected for the reaction between two ions of unlike charge sign. The reaction for the k_1-path is the reaction between neutral (H_2A) and positive ion, $[Fe(phen)_3]^{3+}$. Despite this, the ionic strength dependence was almost the same as that in the reaction of unlike sign. This is probably due to the L-ascorbic acid molecule having a dipole moment.

Calculation of $E_{h.o.m.o.}$ *and* ΔE_T.—Generally, the oxidation potential of a molecule of X may be evaluated theoretically by two calculated properties. One is the energy of the highest occupied molecular orbital of X ($E_{h.o.m.o.}$) which corresponds to the first ionization potential. The other is the difference (ΔE_T) in total electronic energy between the neutral molecule X and its cation X$^+$. The latter property takes into account the effect of electron reorganization during process $X \rightleftharpoons X^+ + e^-$. These two properties usually give consistent results. In the present study both $E_{h.o.m.o.}$ and ΔE_T are calculated for the species H_2A and HA^-. The molecular structure of L-ascorbic acid determined by *X*-ray analysis [8,9] was used for the CNDO/2 MO calculation. The same structure was used for the calculation of E_T of X and X$^+$. The values of $E_{h.o.m.o.}$ and ΔE_T are presented in Table 4, together with other parameters.

DISCUSSION

Since both the ions $[Co(C_2O_4)_3]^{3-}$ and $[Fe(phen)_3]^{3+}$ are one-electron oxidants, the oxidation reactions of L-ascorbic acid by these oxidants could favourably occur with two successive one-electron transfer reactions. Thus, the mechanism (6)—(10) is consistent with the empirical results; $X^n = [Co(C_2O_4)_3]^{3-}$ or $[Fe(phen)_3]^{3+}$.

$$H_2A \overset{K_a}{\rightleftharpoons} HA^- + H^+ \qquad (6)$$

$$X^n + H_2A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2A^{\cdot +} + X^{n-1} \qquad (7)$$

$$X^n + HA^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HA^{\cdot} + X^{n-1} \qquad (8)$$

$$X^n + H_2A^{\cdot +} \xrightarrow{k_3} X^{n-1} + A + 2H^+ \qquad (9)$$

$$X^n + HA^{\cdot} \xrightarrow{k_4} X^{n-1} + A + H^+ \qquad (10)$$

Assuming steady-state concentrations for $H_2A^{\cdot +}$ and $HA^{\cdot}$, and the conditions $k_3[X^n] \gg k_{-1}[X^{n-1}]$ and $k_4[X^n] \gg k_{-2}[X^{n-1}]$ equation (11) can be derived. If $[H^+] \gg K_a$, this gives equation (12). Equations (11) and (12)

$$-d[X^n]/dt = 2\left\{k_1 + (k_2 - k_1)\frac{K_a}{[H^+] + K_a}\right\}[X^n][A_T] \qquad (11)$$

$$-d[X^n]/dt = 2(k_1 + k_2K_a[H^+]^{-1})[X^n][A_T] \qquad (12)$$

correspond to equations (3) and (5) respectively, and therefore are in accordance with the empirical results.

Both complex ions are inert to ligand substitution, and thus the most favourable mechanism of reaction may be of two successive one-electron transfer reactions through an outer-sphere activated complex. The Marcus theory[3] is useful for examining the free energy of activation for the adiabatic outer-sphere redox reactions. According to the Marcus theory, the excess free energy of activation for a cross reaction (ΔG_{12}^*) varies with the standard free-energy change ($\Delta G_{12}^{\ominus}$) for the reactions (13)—(16) where

$$\Delta G_{12}^* = \omega_{12} + \lambda_{12}(1 + \Delta G_{12'}^{\ominus}/\lambda_{12})^2/4 \qquad (13)$$

$$\Delta G_{12'}^{\ominus} = \Delta G_{12}^{\ominus} + \omega_{12} - \omega_{21} \qquad (14)$$

$$\lambda_{12} = 2(\Delta G_{11}^* - \omega_{11} + \Delta G_{22}^* - \omega_{22}) \qquad (15)$$

$$k_{12} = Z \exp(-\Delta G_{12}^*/RT) \qquad (16)$$

ΔG_{11}^* and ΔG_{22}^* are the free energies of activation for the self-exchange electron-transfer reactions, and ω_{11} and ω_{22} represent the work terms involved in the same reactions; ω_{12} and ω_{21} are the work terms required to bring the reactants or products together at the separate distance in the activated complex; Z is the collision frequency in solution, and is usually taken as 10^{11} dm^3 mol^{-1} s^{-1} at 25 °C. The parameter λ_{12} is equal to $\lambda_i + \lambda_0$; where λ_0 is the solvent reorientation term and λ_i is the contribution term from the inner-sphere changes in bond lengths and angles in molecules of the activated states. When λ_i is negligible, λ_{12} is equal to λ_0.

By the same treatments as those reported previously[2] and assuming radii of 350, 450, and 700 pm for L-ascorbic acid,* tris(oxalato)cobaltate(III,II),† and tris(1,10-phenanthroline)iron(III,II)[10] respectively, the values of λ_0 are found to be 97 and 90 kJ mol^{-1} for the reactions of L-ascorbic acid with $[Co(C_2O_4)_3]^{3-}$ and $[Fe(phen)_3]^{3+}$ respectively. Under the conditions of ionic strength of 1.0 mol dm^{-3}, all the work terms except ω_{22} are smaller than 1 kJ mol^{-1} and thus the work terms are totally insignificant in the evaluation of $\Delta G_{12}^{\ominus}$; ω_{22} is 1.22 and 0.08 kJ mol^{-1} for $[Co(C_2O_4)_3]^{3-,4-}$ and $[Fe(phen)_3]^{3+,2+}$ respectively. ΔG_{12}^* is obtained from the rate constants in Table 3. By using the values of ΔG_{12}^*, λ_{12} (λ_i being assumed to be negligible), and the work terms, $\Delta G_{12}^{\ominus}$ can be estimated. $\Delta G_{12}^{\ominus}$ allows the estimation of the standard redox potential. The estimated redox potentials $E^{\circ}(H_2A^{\cdot +}/H_2A)$ and $E^{\circ}(HA^{\cdot}/HA^-)$ are listed in Table 4 together with other kinetic parameters. In the case of the reaction between L-ascorbic acid and $[Co(C_2O_4)_3]^{3-}$, the pre-exponential factor deviates greatly from 10^{11} dm^3 mol^{-1} s^{-1} and thus a non-adiabatic process may be involved.‡ $[Co(C_2O_4)_3]^{3-}$ is a low-spin complex, while the cobalt(II) complex is high-spin. In addition, the energy barrier for the self-exchange reaction between cobalt(III) and cobalt(II) complexes is likely to be large due to the spin multiplicity change accompanying the electron transfer. Thus, the contribution from the inner-sphere reorientation, *i.e.* λ_i, may be large. Due to the above reasons, both values $E^{\circ}(H_2A^{\cdot +}/H_2A)$ and $E^{\circ}(HA^{\cdot}/HA^-)$ estimated from reactions with $[Co(C_2O_4)_3]^{3-}$ were somewhat larger than those from reactions with $[Fe(phen)_3]^{3+}$ (see Table 4). Pelizzetti *et al.*[1] studied the oxidation of L-ascorbic acid by several oxidants and estimated, by the same treatments as those in the present paper, $E^{\circ}(H_2A^{\cdot +}/H_2A) = 1.35$ or 1.40 V and $E^{\circ}(HA^{\cdot}/HA^-) = 0.88$ or 0.93 V. These values are in good agreement with the corresponding values of E^0 which we estimated from the reaction with $[Fe(phen)_3]^{3+}$ (see Table 4). Pelizzetti *et al.*[11] reported that the observed rate constants (k_0) in the reaction between L-ascorbic acid and $[Fe(phen)_3]^{3+}$ were proportional to $[H^+]^{-1}$ without intercept and the k_1 path was not found. Their observation is different from ours. As seen in Figure 2 and from analysis of the data in Table 2, the k_1 path is obviously found in our study, especially in the experiments at higher temperatures and lower ionic strengths. Since the study by Pelizzetti *et al.*[11] was done at an ionic strength of 1.0 mol dm^{-3}, the k_1 path might have been difficult to find. Our value of k_2 under the same conditions of 6.2×10^8 dm^3 mol^{-1} s^{-1} is compared to their value of 7.8×10^8 dm^3 mol^{-1} s^{-1} at an ionic strength of 1.0 mol dm^{-3} at 20 °C (see Table 3). Their slightly larger value may be due to the neglection of the k_1 path from the observed rate constant k_0. The values of $\Delta H_{12}^{\ddagger}$ and $\Delta S_{12}^{\ddagger}$ (and also ΔG_{12}^*) are in good agreement with each other (see Table 4).

When $E_{h.o.m.o.}(H_2A)$ is compared with $E_{h.o.m.o.}(HA^-)$ in Table 4, it is apparent that HA^- is oxidized much more easily than the species H_2A. The same trend is given by the comparison of $\Delta E_T(H_2A^{\cdot +}/H_2A)$ with $\Delta E_T(HA^{\cdot}/HA^-)$. This trend is obviously revealed by the comparison of k_1 and k_2 in Table 3, and by the comparison of $E^{\circ}(H_2A^{\cdot +}/H_2A)$ and $E^{\circ}(HA^{\cdot}/HA^-)$ in Table 4.

---

* This radius ($r = 350$ pm) was calculated using the equation $\frac{4}{3}\pi r^3 = M/N\rho$, where ρ is the density, M the molecular weight, and $N = 6.023 \times 10^{23}$ (from ref. 1).

† This radius (450 pm) is the same as adopted in the work of R. A. Holwerda, D. B. Knaff, H. B. Gray, J. D. Clemmer, R. Crowley, J. M. Smith, and A. G. Mauk, *J. Am. Chem. Soc.*, 1980, **102**, 1142.

‡ The pre-exponential factor is different from the collision frequency [Z in equation (16)]. If we tentatively estimate the pre-exponential factor by using Arrhenius' equation, $k = A \exp(-E_a/RT)$, we get 3×10^{14} and 5×10^7 dm^3 mol^{-1} s^{-1} respectively for reactions of H_2A and HA^- with tris(oxalato)cobaltate(III).

This work was partly supported by a Grant-in-Aid for Scientific Research B (No. 447039) from the Japanese Ministry of Education.

[1/924 *Received, 9th June, 1981*]

REFERENCES

[1] Pelizzetti, E. Mentasti, and E. Pramauro, *Inorg. Chem.*, 1978, **17**, 1181, and refs. therein.

[2] M. Kimura, S. Yamabe, and T. Minato, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1699.

[3] R. A. Marcus, *J. Phys. Chem.*, 1968, **72**, 891, and refs. therein.

[4] J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' MacGraw-Hill, New York, 1970.

[5] S. P. L. Sörensen, *Z. Anorg. Allg. Chem.*, 1896, **11**, 1.

[6] J. C. Bailer, jun., and E. M. Jones, *Inorg. Synth.*, 1939, **1**, 35.

[7] S. Toshima, 'Kiso Denkikagaku,' Asakura–Shoten, Tokyo, 1965, p. 68; J. Kielland, *J. Am. Chem. Soc.*, 1937, **59**, 1675.

[8] Jan Hvoslef, *Acta Crystallogr., Sect. B*, 1968, **24**, 23.

[9] Jan Hvoslef, *Acta Crystallogr., Sect. B*, 1969, **25**, 2214.

[10] B. M. Gordon, L. L. Williams, and N. Sutin, *J. Am. Chem. Soc.*, 1961, **83**, 2061.

[11] E. Pelizzetti, E. Mentasti, and E. Pramauro, *Inorg. Chem.*, 1976, **15**, 2898.