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Outer-Sphere Oxidation of Ascorbic Acid

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Oxidation of ascorbic acid by a number of one-electron-acceptor metal complexes (namely, hexachloro-, hexabromo-, aquopentachloro-, and diaquotetrachloroiridate(IV), octacyanomolybdate(V), dicyanobis(1,10-phenanthroline)-, dicyanobis(2,2′-bipyridine)-, and tetracyano(1,10-phenanthroline)iron(III), tris(5-bromo-1,10-phenanthroline)- and tris(1,10-phenanthroline-5-sulfonic acid)iron(III)) were found to be first order with respect to oxidizing agent concentration and first order in ascorbic acid concentration. The dependence on acidity suggested a rate law of the form $-{}^1/_2\mathrm{d}[\mathrm{Ox}]/\mathrm{d}t = (k_a + k_b[\mathrm{H}^+]^{-1})$[ascorbic acid][Ox], where k_a pertains to the undissociated form of ascorbic acid and k_b to the ascorbate monoanion; the relative contributions of these two paths are related to the reduction potentials and to the intrinsic parameters of the oxidizing agents. Since an outer-sphere mechanism is operating, the observed specific rate constants are discussed in terms of the Marcus theory. Comparison among oxidizing agents with different intrinsic parameters and with data concerning oxidation of benzene-1,2-diols suggests that an electron-transfer mechanism is operating. An estimation of the reduction potentials of the $H_2A^+\cdot/H_2A$ and $HA\cdot/HA^-$ couples (H_2A represents ascorbic acid) has been attempted. The effect of ionic strength and temperature has been investigated.

Introduction

In a previous paper[1] the kinetics of the oxidation of ascorbic acid by tris(1,10-phenanthroline)iron(III) and its derivatives (later referred to as $Fe^{III}L_3$) was investigated and an outer-sphere electron-transfer mechanism was advanced. Moreover, the estimation of some thermodynamic parameters was attempted by applying the Marcus cross relationship.[2] The present paper deals with the kinetics and mechanism of oxidation of ascorbic acid by a series of oxidizing agents in order to achieve additional information on this important system.

Table I. Experimental Conditions for the Investigated Systems

Oxidizg agent	Monitored species	Wave-length, nm	ϵ^h	Acidity range	Temp, °C
$IrCl_6^{2-}$	$IrCl_6^{2-}$	478[a]	4070	0.10–1.00	6, 20
$Ir(H_2O)Cl_5^-$	$Ir(H_2O)Cl_5^-$	450[b]	3320	0.30–1.00	6, 20
$Ir(H_2O)_2Cl_4$	$Ir(H_2O)_2Cl_4$	445[c]	2920	0.30–1.00	6, 20
$IrBr_6^{2-}$	$IrBr_6^{2-}$	585[d]	3800	0.30–1.00	6, 20
$Mo(CN)_8^{3-}$	$Mo(CN)_8^{3-}$	388[e]	1280	0.10–1.00	6, 20, 35
$Fe(phen)_2(CN)_2^+$	$Fe(phen)_2(CN)_2$	500[f]	6000	0.30–1.00	20, 35
$Fe(bpy)_2(CN)_2^+$	$Fe(bpy)_2(CN)_2$	492[f]	4700	0.30–1.00	20, 35
$Fe(phen)(CN)_4^-$	$Fe(phen)(CN)_4^{2-}$	424[f]	3220	0.30–1.00	20, 35
$Fe(sphen)_3^{3+}$	$Fe(sphen)_3^{2+}$	512[g]	12240	0.40–1.00	6, 20
$Fe(bphen)_3^{3+}$	$Fe(bphen)_3^{2+}$	515[g]	12500	0.40–1.00	6, 20

[a] Reference 48. [b] Reference 3. [c] Reference 4. [d] Reference 49. [e] Reference 50. [f] Reference 51. [g] Reference 52. [h] L mol^{-1} cm^{-1}.

Experimental Section

Reagents. Sodium hexachloroiridate(IV) and sodium hexachloroiridate(III) were supplied by Merck and Alfa Inorganics, respectively. Sodium aquopentachloroiridate(III) solutions were prepared by aquating a sample of $IrCl_6^{3-}$ in acid solution at 40–45 °C for ca. 2 h,[3] and these solutions were anodically oxidized in order to obtain aquopentachloroiridate(IV). Sodium diaquotetrachloroiridate(III) was prepared by aquation of $IrCl_6^{3-}$ solutions at 100 °C for 2 min;[4] the corresponding Ir(IV) compound was obtained by anodic oxidation at a platinum electrode. The spectral data of the resulting Ir(IV) species agreed with literature data.[3,4] Sodium hexabromoiridate(IV) was supplied by Platinum Co. Sodium octacyanomolybdate(IV) was prepared according to published procedures[5] and the corresponding Mo(V) derivative was obtained by anodic oxidation. Dicyanobis(1,10-phenanthroline)iron(II) and dicyanobis(2,2′-bipyridine)iron(II) were supplied by Eastman and potassium tetracyano(1,10-phenanthroline)iron(II) by K & K; the corresponding iron(III) species were obtained by electrooxidation. Tris(1,10-phenanthroline-5-sulfonic acid)iron(II) and tris(5-bromo-1,10-phenanthroline)iron(II) were obtained according to our procedure;[1] the corresponding iron(III) species were prepared by addition of stoichiometric quantities of cerium(IV) sulfate.[6] Ascorbic acid, adrenaline, perchloric acid, and sodium and lithium perchlorate were supplied by Merck. 3,4-Dihydroxybenzonitrile was obtained from K & K.

Kinetic Measurements. The kinetic experiments were carried out with a Durrum-Gibson stopped-flow spectrophotometer by following, at the proper wavelength (see Table I), the disappearance of the oxidizing agent or the formation of the reduced form. The acidity ranges ($HClO_4$) are reported in Table I, and the ionic strength was kept constant at 1.0 M by addition of $NaClO_4$ (a series of runs were performed also with $LiClO_4$: no significant differences were observed). The ascorbic acid concentrations were kept high (≥10-fold with respect to the oxidizing agent concentration) in order to ensure pseudo-first-order conditions. In the faster reactions, second-order conditions were found necessary. The observed rate constants were evaluated by treating the points of a single run with a weighted least-squares method.[7] In the estimation of the other kinetic parameters, weights were assigned based on the standard deviation of the single kinetic runs (3–6%).

Potentiometric Measurements. The first acid dissociation constant of ascorbic acid at different ionic strengths and solvent compositions was determined by potentiometric titrations with a Metrohm E 388 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 was calculated from these pH measurements. Activity coefficients were evaluated by means of the Davies equation.[8] The solutions of ascorbic acid were prepared with air-free distilled water, and purified nitrogen was bubbled through the cell during each titration.

Results

Stoichiometry. By maintaining a slight excess of oxidizing agent and by performing spectrophotometric measurements at the proper wavelength, the following stoichiometric equation was found to hold for all the oxidants:

$$2\mathrm{Ox} + H_2A \rightarrow 2\mathrm{Red} + A + 2H^+ \qquad (1)$$

where H_2A and A represent ascorbic and dehydroascorbic acid, respectively. Further, dehydroascorbic acid was also experimentally detected as the final product.[9]

Dissociation Constants. The dissociation constants for the equation $H_2A \rightleftharpoons HA^- + H^+$ were evaluated at different ionic strengths. They are as follows, with ionic strength in parentheses: at 6.0 °C, 3.9 × 10^{-5} (0.05), 5.5 × 10^{-5} (0.10), 5.7 × 10^{-5} (0.30), 6.0 × 10^{-5} M (0.50); at 20.0 °C, 7.1 × 10^{-5} (0.05), 8.1 × 10^{-5} (0.10), 8.4 × 10^{-5} M (0.15).

Kinetics of Reaction. When pseudo-first-order conditions are chosen, plots of ln $(A_\infty - A_t)$ (or ln $(A_t - A_\infty)$) vs. time are linear for at least 80% completion (A_∞ and A_t represent the absorbance at equilibrium and at time t, respectively). Moreover, the observed first-order rate constants show also

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Table II. Second-Order Rate Constants (L mol^{-1} s^{-1}) at 20.0 °C and at Different Acidities ($\mu = 1.0$ M)

	[H$^+$], M						
Oxidizg agent	0.10	0.15	0.20	0.30	0.50	0.70	1.00
$IrCl_6^{2-}$ ($\times 10^{-3}$)			13	8.8	5.7	4.0_5	2.9_5
$Ir(H_2O)Cl_5^-$ ($\times 10^{-4}$)				8.7_5	5.4	3.9_5	2.9
$Ir(H_2O)_2Cl_4$ ($\times 10^{-5}$)				7.2	5.1	3.8	3.1
$IrBr_6^{2-}$ ($\times 10^{-3}$)				18	11	8.0	5.5
$Mo(CN)_8^{3-}$ ($\times 10^{-2}$)	$13._5$	9.1	7.0	4.6	2.8	2.0	1.3_5
$Fe(phen)_2(CN)_2^+$ ($\times 10^{-2}$)				$17._5$	11	7.9_5	$5._6$
$Fe(bpy)_2(CN)_2^+$ ($\times 10^{-2}$)				6.7	4.2	2.9	2.1_5
$Fe(phen)(CN)_4^-$				12.8	8.4_5	5.7	4.3
$Fe(sphen)_3^{3+}$ ($\times 10^{-6}$)				1.45^a	1.3^b	1.15^c	1.05
$Fe(bphen)_3^{3+}$ ($\times 10^{-5}$)				10.5	9.0	8.1	6.9
$Mo(CN)_8^{3-}$ ^{d} ($\times 10^{-2}$)	11		5.5	3.8	2.4	1.8	

[a] 0.40 M ($HClO_4$). [b] 0.60 M ($HClO_4$). [c] 0.80 M ($HClO_4$). [d] $\mu = 1.0$ M ($LiClO_4$).

a linear dependence on ascorbic acid concentration. When second-order conditions were adopted, second-order plots were also linear for 75% completion, thus confirming the first-order dependence on both reagents.

The second-order rate constants k_0 increase with decreasing acidity and plots of k_0 vs. $[H^+]^{-1}$ are straight lines with intercepts that, in some cases, differ significantly from zero. Thus, the following empirical rate law can be suggested:

$$-{}^1/_2 d[Ox]/dt = k_0[Ox][H_2A] = (k_a + k_b[H^+]^{-1})[Ox][H_2A] \qquad (2)$$

Values of k_0 obtained at 20.0 °C are collected in Table II. The data for the reactions of adrenaline and 3,4-dihydroxybenzonitrile with $Fe(sphen)_3^{3+}$ and $Fe(bphen)_3^{3+}$ at 1.00 M [$HClO_4$] showed that the reaction were second order overall.

Effect of the Reduced Forms. Some kinetic runs were performed in the presence of reduced species of metal complexes, namely, $IrCl_6^{3-}$, $Ir(H_2O)Cl_5^{2-}$, $Ir(H_2O)_2Cl_4^-$, $IrBr_6^{3-}$, and $Mo(CN)_8^{4-}$, in concentrations up to 10 times that of the corresponding oxidized forms. No significant effect was observed on the calculated rate constants.

Effect of Ionic Strength. In order to investigate the ionic strength effect, kinetic runs were performed at low acidity with increasing addition of $NaClO_4$ up to 0.60 M. The observed second-order rate constants k_0 are listed in Table III. Although the ionic strengths employed in these experiments lie well outside the Debye–Hückel region, the ionic strength dependence is qualitatively as expected for the charges involved.[10]

Discussion

The investigated complex ions are all one-electron oxidizing agents and thus the present noncomplementary reactions can be described by the sequence

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

$$Ox + H_2A \xrightarrow{k_2} \text{radical} + \text{Red} \qquad (4)$$

$$Ox + HA^- \xrightarrow{k_3} \text{radical} + \text{Red} \qquad (5)$$

$$Ox + \text{radical} \xrightarrow{\text{fast}} A + \text{Red} + nH^+ \qquad (6)$$

where n is 1 or 2. The presence of free radicals in the oxidation of ascorbic acid was confirmed by ESR measurements and kinetic considerations.[11,12] Equations 3–6 lead to rate law 7

$$-{}^1/_2 d[Ox]/dt = (k_2 + k_3K_1[H^+]^{-1})[Ox][H_2A] \qquad (7)$$

(with ascorbic acid essentially in the form H_2A in the presently investigated conditions). The linearity of first-order plots and the absence of an effect of the presence of reduced species indicate that no reverse reactions are kinetically relevant. Thus, by comparing eq 7 with the experimental rate law 2, it follows that $k_a = k_2$ and $k_b = k_3K_1$ (see Table IV). Comparison of the presently observed activation parameters and rate constants with those for displacement of ligands from the coordination spheres of metal centers[13] suggests that the electron-transfer occurs through an outer-sphere activated

Table III. Ionic Strength Effect: Second-Order Rate Constants (L mol^{-1} s^{-1}) at [$HClO_4$] = 0.10 M, 20.0 °C

	μ, M ($NaClO_4$)								
Oxidizg agent	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.50	0.60
$IrCl_6^{2-}$ ($\times 10^{-3}$)	9.2	10.5	12.5	14	15.5				
$Ir(H_2O)Cl_5^-$ ($\times 10^{-5}$)^a		1.0	1.05	1.1	1.2		1.2	1.3	1.35
$Ir(H_2O)_2Cl_4$ ($\times 10^{-6}$)^a		1.3	1.2	1.4	1.5		1.5	1.7	1.5
$IrBr_6^{2-}$ ($\times 10^{-4}$)	1.85	2.45	2.7	2.9	3.0		3.1		4.1
$Mo(CN)_8^{3-}$ ($\times 10^{-2}$)^b	6.65	8.3	10.5	12		15			20
$Fe(phen)_2(CN)_2^+$ ($\times 10^{-4}$)	2.2	2.05	1.7	1.5	1.45		1.4		1.05
$Fe(bpy)_2(CN)_2^+$ ($\times 10^{-3}$)	5.9	5.3	5.0	4.3	4.0		3.6		2.7
$Fe(phen)(CN)_4^-$	36	39	41	42	46				
$Fe(mphen)_3^{3+}$ ($\times 10^{-6}$)	3.0	1.9	1.6	1.3	1.1			0.69	

[a] 6.0 °C. [b] $[H^+] = 0.05$ M. Other data: $\mu = 0.05, k = 4.3 \times 10^2$; $\mu = 0.06, k = 4.8 \times 10^2$; $\mu = 0.07, k = 5.4 \times 10^2$; $\mu = 0.09, k = 6.4 \times 10^2$; $\mu = 0.12$ M, $k = 7.05 \times 10^2$ L mol^{-1} s^{-1}.

Table IV. Specific Rate Constants for the Oxidation of Ascorbic Acid by Different Complex Ions ($\mu = 1.0$ M)

Oxidizg agent	k_2(6.0 °C)^a	k_2(20.0 °C)	ΔH^* ^{b}	ΔS^* ^{c}	k_3(6.0 °C)	k_3(20.0 °C)	ΔH^* ^{b}	ΔS^* ^{c}
$IrCl_6^{2-}$	Ca. 3×10^2	Ca. 4×10^2			2.4×10^7	2.8×10^7	1.2	−20
$Ir(H_2O)Cl_5^-$	Ca. 5×10^3	Ca. 5×10^3			2.5×10^8	2.6×10^8	−0.1	−20
$Ir(H_2O)_2Cl_4$	1.0×10^5	1.05×10^5	0.0	−36	2.1×10^9	2.05×10^9 ^{d}		
$IrBr_6^{2-}$	$\leqslant 1 \times 10^2$	$\leqslant 2 \times 10^2$			5.0×10^7	5.9×10^7	1.3	−18
$Mo(CN)_8^{3-}$	$\leqslant 10$	$\leqslant 15$			1.5×10^6	1.45×10^6 ^{e}	−0.2	−31
$Fe(phen)_2(CN)_2^+$	Ca. 40^f	Ca. 1×10^2 ^{g}			7.9×10^6 ^{f}	8.3×10^6 ^{g}	0.0	−27
$Fe(bpy)_2(CN)_2^+$	$\leqslant 10^f$	Ca. 30^g			3.2×10^6 ^{f}	4.0×10^6 ^{g}	2.1	−22
$Fe(phen)(CN)_4^-$	Ca. 0.6^f	Ca. 1.5^g			4.0×10^4 ^{f}	4.8×10^4 ^{g}	1.6	−32
$Fe(sphen)_3^{3+}$	6.6×10^5	7.6×10^5	1.0	−28	2.7×10^9	3.2×10^9 ^{d}		
$Fe(bphen)_3^{3+}$	3.9×10^5	4.6×10^5	1.3	−28	2.1×10^9	2.8×10^9 ^{d}		

[a] L mol^{-1} s^{-1}. [b] kcal mol^{-1}; the error is ±0.7–1.2 kcal mol^{-1}. [c] cal deg^{-1} mol^{-1}; the error is ±2.3–4.0 cal deg^{-1} mol^{-1}. [d] The reported values include also the diffusion contribution. [e] A value 1.6×10^6 has been determined at 35.0 °C. [f] 20.0 °C. [g] 35.0 °C.

Table V. Comparison of Kinetic Data for the Oxidation of Undissociated Ascorbic Acid and Benzene-1,2-diols ($\mu = 1.0$ M, 20.0 °C)

Oxidizg agent	Ascorbic acid	Adrenaline	3,4-Dihydroxy-benzoic acid	3,4-Dihydroxy-benzonitrile
$Fe(nphen)_3^{3+}$	3.8×10^6 [a]	$>10^8$ [b]	Ca. 2.7×10^7 [b,c]	3.1×10^6 [b,c]
$Fe(sphen)_3^{3+}$	7.6×10^5 [d]	Ca. 2×10^7 [d,e]		2.8×10^5 [d]
$Fe(bphen)_3^{3+}$	4.6×10^5 [d]	Ca. 1×10^7 [d,e]		1.9×10^5 [d]
$Fe(cphen)_3^{3+}$	2.0×10^5 [a]			
$Fe(phen)_3^{3+}$	3.0×10^4 [a]	1.15×10^6 [b,c]	6.0×10^4 [b,c]	1.2×10^4 [b,c]
$Fe(mphen)_3^{3+}$	$<1 \times 10^4$ [a]	4.2×10^5 [b,c]	2.1×10^4 [b,c]	3.2×10^3 [b,c]
$IrCl_6^{2-}$	Ca. 4×10^2 [d]	5.4×10^3 [c,f]	7.1×10^1 [c,f]	1.54×10^1 [c,f]
$Ir(H_2O)Cl_5^-$	5×10^3 [d]	8.9×10^4 [c,g]	2.7×10^3 [c,g]	7.2×10^2 [c,g]
$Ir(H_2O)_2Cl_4$	1.05×10^5 [d]	7.8×10^5 [c,g]	3.2×10^4 [c,g]	8.6×10^3 [c,g]
$IrBr_6^{2-}$	$<2 \times 10^2$ [d]	3.6×10^3 [c,g]		
$CoW_{12}O_{40}^{5-}$	7.74×10^1 [c,h]	9.5×10^2 [c,h,i]		
$Mn^{3+}(aq)$	6.0×10^3 [j]	2.7×10^3 [k]		
$MnOH^{2+}(aq)$	5.3×10^4 [j]	2.0×10^4 [k]		
$Co^{3+}(aq)$	2.8×10^2 [c,l]	1.6×10^2 [c,m]		
$CoOH^{2+}(aq)$	7.3×10^5 [c,l]	2.0×10^5 [c,m]		

[a] Reference 1. [b] Reference 39b. [c] 25.0 °C. [d] This work. [e] 6.0 °C. [f] Reference 39a. [g] Reference 20. [h] Reference 34. [i] Catechol ($E°$ for catechol is ca. 0.02 V lower than that for adrenaline). [j] Reference 35. [k] Reference 38. [l] Reference 33. [m] Reference 37.

complex in every case. Accordingly, in the present systems the same mechanism previously advanced for the ascorbic acid oxidation by $Fe^{III}L_3$ is operating.[1] In our previous investigation, we reported on the application of the Marcus theory[2] which allowed an estimate of the formal reduction potential $E°(HA\cdot/HA^-)$ as well as the intrinsic parameter $\Delta G^*(HA\cdot/HA^-)$ (that is, the free energy of activation for the self-exchange of HA· with HA^-).

The functional form of the Marcus cross relationship is

$$\Delta G^*_{12} = w_{12} + \lambda(1 + \Delta G°_{12}'/\lambda)^2/4 \tag{8}$$

where $k = Z \exp(-\Delta G^*_{12}/RT)$, Z being the collision frequency in solution (10^{11} L mol^{-1} s^{-1}); λ is defined as $2(\Delta G^*_{11} - w_{11} + \Delta G^*_{22} - w_{22})$, where ΔG^*_{11} and ΔG^*_{22} refer to the self-exchange reactions of the reagents and w_{11} and w_{22} represent the work terms involved in the same reactions; and $\Delta G°_{12}' = \Delta G°_{12} + w_{21} - w_{12}$, where $\Delta G°_{12}$ is the free-energy change of reaction for the prevailing medium and temperature and w_{21} and w_{12} are the work terms required to bring the products or reactants together at the separation distance in the activated complex.

The work terms, arising from Coulombic forces, correspond to

$$w = \frac{z_1 z_2 e^2}{D_s r} \exp(-\kappa r^*) \tag{9}$$

where z_1 and z_2 are the formal charges of reactants, e is the electron charge, D_s is the static dielectric constant, r^* is the distance between the reactants in the activated complex, and the exponential coefficient is the Debye–Hückel term with κ as the reciprocal Debye radius. The terms w_{12} and w_{21} are small in the present ionic strength conditions.

The application of the Marcus theory to reactions involving organic substrates[14] as well as to those between inorganic ions and organic substrates[15] has given satisfactory results. When an homologous series of reactions is investigated, it is possible to evaluate the reorganizational parameter λ, without knowledge of the contributions ΔG^{**}_{11} and ΔG^{**}_{22} (where $\Delta G^{**} = \Delta G^* - w$). In the presently investigated systems, with the series of $Fe^{III}L_3$, a value of $\lambda = 14$ kcal mol^{-1} was adopted (arising from $\Delta G^{**} = 3$ for $Fe^{III}L_3/Fe^{II}L_3$ self-exchange and $\Delta G^{**} = 4$ for $HA\cdot/HA^-$, value derived from reaction rates between radicals and parent molecules); these values led to an estimate of 0.93 V for $E°$ $(HA\cdot/HA^-)$.[1]

For some of the presently investigated oxidants the intrinsic parameter ΔG^{**} is not known (this is the case for Ir(IV) derivatives, with the exception of $IrCl_6^{2-}$, whose ΔG^* is known[16] and also for the mixed cyano–phenanthroline complexes of Fe(III), whose ΔG^* are derived from Marcus theory applications[17]). Moreover, even when ΔG^* of self-exchange is known, some questions arise in the estimation of the work terms.

In a first approximation the λ values which satisfy the reactions with benzenediols can be adopted, namely, 26 kcal mol^{-1} for $IrCl_6^{2-}$,[15b,15c,18,19] $Ir(H_2O)Cl_5^-$, and $Ir(H_2O)_2Cl_4$,[18,20] 16 kcal mol^{-1} for $Fe^{III}L_3$,[21] 21 kcal mol^{-1} for $IrBr_6^{2-}$,[20,23] 21 kcal mol^{-1} for $Mo(CN)_8^{3-}$,[24-27] and 30 kcal mol^{-1} for $Fe(CN)_6^{3-}$.[28] For $Fe(phen)_2(CN)_2^+$ and $Fe(bpy)_2(CN)_2^+$, owing to the similarity with $Fe^{III}L_3$ reactions,[27] a similar value to that of $Fe^{III}L_3$ can be adopted; for $Fe(phen)(CN)_4^-$ a higher value (21 kcal mol^{-1}) can be assumed by comparison with the other compounds.[17]

Acid-Independent Path. The previous investigations on ascorbic acid oxidation pointed out that the main reaction path involves the ascorbate anion.[1,32] Also $Fe^{III}L_3$ derivatives largely confirmed these findings, although tris(5-nitro-1,10-phenanthroline)iron(III) showed different behavior (reaction rates scarcely dependent on acidity); no definitive assessment was possible for the reaction mechanism of this complex.

Among the presently investigated oxidizing ions, some exhibit an acid-independent path which can then be attributed to an electron transfer involving H_2A species.

Recently, data on the oxidation on ascorbic acid by other systems have been obtained, namely, $Co^{III}(aq)$,[33] $Co^{III}W_{12}O_{40}^{5-}$,[34] and $Mn^{III}(aq)$.[35] With aquo ions such as Co(III) and Mn(III), the species $Co^{3+}(aq)$ and $CoOH^{2+}(aq)$, as well as $Mn^{3+}(aq)$ and $MnOH^{2+}(aq)$, have been found to be reactive toward H_2A species only. For the metal-ion-hydrolyzed species a limiting mechanism can be advanced,[36] while for the unhydrolyzed ones mechanisms involving simple electron transfer or more complex paths can be suggested. It is useful to compare the data with those concerning benzene-1,2-diols (whose structure of vicinal diols resembles that of ascorbic acid). Whereas adrenaline and ascorbic acid show similar reactivity toward $Co^{3+}(aq)$ and $Mn^{3+}(aq)$,[37,38] there is observed quite an enhanced reactivity (a factor of 10–100) for adrenaline over ascorbic acid in reaction with $Fe^{III}L_3$ and Ir(IV).[39] Conversely, the reaction rates of H_2A with these last oxidants are quite similar to the ones of 3,4-dihydroxybenzoic acid and 3,4-dihydroxybenzonitrile (see Table V).[39] A possible hypothesis is that a mechanism involving a simple outer-sphere electron abstraction is the main mechanism with the presently investigated oxidants, while a different mechanism is operating with the aquo ions.

From eq 8, by knowing λ, it is possible to estimate the free energy of reaction involved in the rate-determining step and

Table VI. Acid-Independent Path in the Oxidation of Ascorbic Acid ($\mu = 1.0$ M)

Oxidizg agent	$E°$ [a]	k_2 [b]	k_{calcd} [b]	
$Fe(nphen)_3^{3+}$	1.25[e]	3.8×10^6	1.2×10^7 [c]	8.7×10^6 [d]
$Fe(sphen)_3^{3+}$	1.20[e]	7.6×10^5	3.9×10^6 [c]	2.4×10^6 [d]
$Fe(bphen)_3^{3+}$	1.12[e]	4.6×10^5	5.2×10^5 [c]	2.7×10^5 [d]
$Fe(cphen)_3^{3+}$	1.11[e]	2.0×10^5	4.0×10^5 [c]	2.0×10^5 [d]
$Fe(phen)_3^{3+}$	1.06[e]	Ca. 3×10^4	1.0×10^5 [c]	4.5×10^4 [d]
$Fe(mphen)_3^{3+}$	1.02[e]	$\leq 1 \times 10^4$	3.2×10^4 [c]	1.3×10^4 [d]
$IrCl_6^{2-}$	0.957[f]	Ca. 4×10^2	1.5×10^2 [c]	8.2×10^1 [d]
$Ir(H_2O)Cl_5^-$	1.088[f]	Ca. 5×10^3	4.4×10^3 [c]	2.8×10^3 [d]
$Ir(H_2O)_2Cl_4$	1.203[f]	1.2×10^5	6.4×10^4 [c]	4.7×10^4 [d]
$IrBr_6^{2-}$	0.882[f]	$\leq 2 \times 10^2$	1.1×10^2 [c]	4.1×10^1 [d]
$CoW_{12}O_{40}^{5-}$	1.00[g]	7.74×10^1 [h]	9.4×10^1 [c,h]	5.8×10^1 [d,h]

[a] V. [b] L mol^{-1} s^{-1}; 20.0 °C. [c] $E°(H_2A^{+}\cdot/H_2A) = 1.35$ V, $\lambda(Fe^{III}L_3) = 16$ kcal mol^{-1}, and the other data are as described in the text. The values of $E°(FeL_3^{3+/2+})$ could be lower. E.g., for $Fe(sphen)_3^{3+/2+}$ a value 0.04 V lower is reported for 1 M $HClO_4$ with respect to 1 M H_2SO_4; this would give $k = 1.4 \times 10^6$. [d] $E°(H_2A^{+}\cdot/H_2A) = 1.40$ V; λ's decreased by 2 kcal mol^{-1}. [e] Reference 52. [f] Reference 53. [g] Reference 34. [h] 25.0 °C.

consequently the reduction potential of $H_2A^+\cdot/H_2A$ couple. If the intrinsic parameters (i.e., the electron self-exchange rates) for $H_2Q^+\cdot/H_2Q$ (where H_2Q represents the benzenediols) and $H_2A^+\cdot/H_2A$ are the same, then the λ which satisfy the benzenediols can be adopted for H_2A. No experimental data are available for these exchange rates; for $H_2Q^+\cdot/H_2Q$ systems, an estimate of ΔG^{**} can be attempted with the knowledge of ΔG^{**} for the couples $IrCl_6^{2-/3-}$, $FeL_3^{3+/2+}$, and $Mo(CN)_8^{3-/4-}$. In turn, the estimation of these parameters for oxidizing agents is complicated by the difficulties in the estimation of the work terms. As reported in footnotes 18 and 19, $\Delta G^{**} \leq 6.5$ kcal mol^{-1} can be proposed as a probable limit for the intrinsic parameter of $H_2Q^+\cdot/H_2Q$ ($\geq 2 \times 10^6$ L mol^{-1} s^{-1} for self-exchange rate).[19] Both for the reasons outlined in footnote 19 and owing to the fact that other exchange rates between radicals and parent molecules are much higher than 2×10^6 L mol^{-1} s^{-1},[14] smaller values of λ must also be considered. For example, from the data concerning $Fe(bphen)_3^{3+}$ ($\Delta G^{**}_{12} = 7.15$ kcal mol^{-1} for the undissociated ascorbic acid) and by assuming $\lambda = 16$ kcal mol^{-1}, one calculates $\Delta E° = -0.23$ V (that is, $E°(H_2A^+\cdot/H_2A) = 1.35$ V). By assuming $\lambda = 14$ kcal mol^{-1}, $\Delta E° = -0.26$ V and $E°(H_2A^+\cdot/H_2A) = 1.38$ V; this leads to values of $E°(H_2A^+\cdot/H_2A)$ (averaged on the data of seven oxidants in Table VI) of 1.36 ± 0.04 V (by adopting the same λ found for benzenediols) and 1.40 ± 0.03 V (with λ's decreased by 2 kcal mol^{-1}). The two columns of calculated constants in Table VI were obtained by assuming the limits 1.35–1.40 V for $E°$ and the same λ used for benzenediols (column c) or λ lower by 2 kcal mol^{-1} (column d).

It is also possible to compare the data obtained by McAuley et al. in the oxidation of ascorbic acid, quinol, and catechol with $Co^{III}W_{12}O_{40}^{5-}$.[34] In fact, this outer-sphere oxidizing ion[40] reacts with dissociated and undissociated ascorbic acid. From the kinetic data for benzenediol oxidation (by assuming formation of $H_2Q^+\cdot$ species as reaction product of the rate-determining step and $E°(Co^{III}/Co^{II}) = 1.00$ V),[34] a value of $\lambda = 31$ kcal mol^{-1} can be derived: this value leads to a calculated value of 94 L mol^{-1} s^{-1} for the reaction with H_2A (by assuming $E°(H_2A^+\cdot/H_2A) = 1.35$ V) to be compared with the experimental one of 77.4 L mol^{-1} s^{-1}. It must be noted that the estimated λ value for $Co^{III}W_{12}O_{40}^{5-}$ reactions should give a value for the self-exchange reaction rate $CoW_{12}O_{40}^{5-/6-}$ comparable with the experimental observations. In fact, it follows that $\Delta G^{**} = 8.5$–9.5 kcal mol^{-1}, while a value $\Delta G^* = 15.6$, at 25 °C and $\mu = 0.05$ M, is determined experimentally,[41] which leads to $\Delta G^{**} = 9.5$ kcal mol^{-1} ($r = 5$ Å).

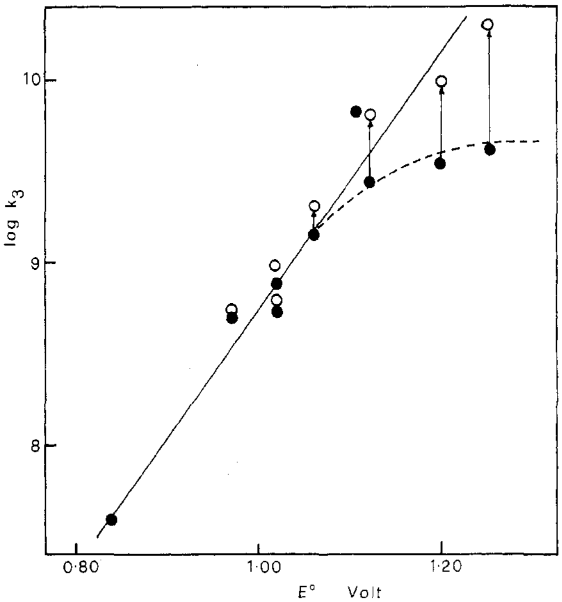

Figure 1. log k_3 vs. $E°$ for the oxidation of ascorbate anion with $Fe^{III}L_3$: (●) experimental points; (○) k_{act}, calculated with eq 10, by assuming $k_{\text{diff}} = 5 \times 10^9$ L mol^{-1} s^{-1} (see text).

Acid-Dependent Path. This reaction path involves interaction between the oxidizing agents and the dissociated species of ascorbic acid. The specific rate constants with $Fe^{III}L_3$ are very high and approach those of diffusion-controlled reactions; in order to eliminate the diffusional contribution from the measured value, eq 10[2] can be used, where k_{diff} is the dif-

$$1/k_{\text{obsd}} = 1/k_{\text{diff}} + 1/k_{\text{act}} \tag{10}$$

fusion-controlled rate constant and k_{act} the activation-controlled rate constant. The term k_{diff} could be estimated according to different formulas,[42] whose applicability to the present ionic strength conditions are rather uncertain. If a value 5×10^9 L mol^{-1} s^{-1} is assumed, satisfactory linearity of a plot of log k_{act} vs. $E°(Fe^{III}L_3/Fe^{II}L_3)$ is obtained (see Figure 1).

For deriving the reduction potential of the $HA\cdot/HA^-$ couple, it must be noted that in the present system the difference with the intrinsic parameter concerning $H_2Q^+\cdot/H_2Q$ could be significant, probably more than with respect to $H_2A^+\cdot/H_2A$ (for example, values in the range (0.5–2) × 10^8 L mol^{-1} s^{-1} have been determined in the exchange between quinones and their radical anions).[14] Consequently λ values lower than those observed for benzenediols by up to 4.5 kcal mol^{-1} were considered. By comparing oxidants with different $E°$ and ΔG^{**}, it is then possible to obtain some information on the characteristic parameters of the $HA\cdot/HA^-$ couple. For example, the following values for $E°(HA\cdot/HA^-)$ (in V) are obtained from eq 8 at different λ's (in kcal mol^{-1}). $Fe(bphen)_3^{3+}$: λ = 16, $E°(HA\cdot/HA^-) = 0.87$; λ = 14, $E° = 0.93$; λ = 11.5, $E° = 1.00$. $Fe(dmbpy)_3^{3+}$: λ = 16, $E° = 0.89$; λ = 14, $E° = 0.93$; λ = 11.5, $E° = 0.97$. $IrCl_6^{2-}$: λ = 26, $E° = 0.80$; λ ≈ 24, $E° = 0.84$; λ = 21.5, $E° = 0.90$. $IrBr_6^{2-}$: λ = 21, $E° = 0.80$; λ = 19, $E° = 0.84$; λ = 16.5, $E° = 0.90$. $Mo(CN)_8^{3-}$: λ = 21, $E° = 0.90$; λ = 19, $E° = 0.94$; λ = 16.5, $E° = 0.98$. Then, by adopting the same λ's as for benzenediols, $E°(HA\cdot/HA^-) = 0.88 \pm 0.07$ V is obtained; if the λ values are decreased by 2 kcal mol^{-1}, $E° = 0.92 \pm 0.06$ V whereas a decrease of 4.5 kcal mol^{-1} gives $E° = 0.98 \pm 0.05$ V (these values are averaged on 18 systems listed in Table VII). It can be seen that the value of $E°(HA\cdot/HA^-)$ should lie reasonably in the range 0.85–1.00 V.

The data reported in Table VII are then calculated with two sets of values for λ and $E°$, for comparison purposes. By considering the involved approximation (particularly for k_{diff}

Table VII. Acid-Dependent Path in the Oxidation of Ascorbic Acid ($\mu = 1.0$ M)

Oxidizg agent	$E°$ [a]	k_3 [b]	k_{act} [c]	k_{calcd} [b]	
$Fe(nphen)_3^{3+}$	1.25[f]	4×10^9 [k]	2×10^{10}	2.2×10^{10} [d]	2.6×10^{10} [e]
$Fe(sphen)_3^{3+}$	1.20[f]	3.2×10^9 [l]	9×10^9	1.3×10^{10} [d]	1.5×10^{10} [e]
				(8.6×10^9)[d,q]	(9.7×10^9)[e,q]
$Fe(bphen)_3^{3+}$	1.12[f]	2.8×10^9 [l]	6×10^9	5.2×10^9 [d]	5.8×10^9 [e]
$Fe(cphen)_3^{3+}$	1.11[f]	7×10^9 [k,m]		4.6×10^9 [d]	5.1×10^9 [e]
$Fe(phen)_3^{3+}$	1.06[f]	1.5×10^9 [k]	2×10^9	2.3×10^9 [d]	2.4×10^9 [e]
$Fe(mphen)_3^{3+}$	1.02[f]	7.9×10^8 [k]	9.4×10^8	1.2×10^9 [d]	1.3×10^9 [e]
$Fe(dmphen)_3^{3+}$	0.97[f]	5.3×10^8 [k]	5.9×10^8	5.5×10^8 [d]	5.3×10^8 [e]
$Fe(bpy)_3^{3+}$	1.02[g]	5.4×10^8 [n]	6.0×10^8	1.2×10^9 [d]	1.3×10^9 [e]
$Fe(dmbpy)_3^{3+}$	0.84[g]	3.9×10^7 [n]	3.9×10^7	4.5×10^7 [d]	3.6×10^7 [e]
$Fe(phen)_2(CN)_2^+$	0.80[f]	8.3×10^6 [l]	8.3×10^6	1.9×10^7 [d]	1.4×10^7 [e]
$Fe(bpy)_2(CN)_2^+$	0.78[f]	4.0×10^6 [l]	4.0×10^6	1.2×10^7 [d]	8.7×10^6 [e]
$Fe(phen)(CN)_4^-$	0.69[f]	4.8×10^4 [l]	4.8×10^4	1.9×10^5 [d]	5.6×10^4 [e]
$Fe(CN)_6^{3-}$	0.71[h]	8.6×10^2 [o]	8.6×10^2	7.0×10^3 [d]	5.1×10^3 [e]
$IrCl_6^{2-}$	0.957[i]	2.8×10^7 [l]	2.8×10^7	6.1×10^6 [d]	5.6×10^6 [e]
$Ir(H_2O)Cl_5^-$	1.088[i]	2.6×10^8 [l]	2.7×10^8 [p]	5.9×10^7 [d]	6.0×10^7 [e]
$Ir(H_2O)_2Cl_4$	1.203[i]	2.0×10^9 [l]	3.3×10^9 [p]	3.3×10^8 [d]	3.6×10^8 [e]
$IrBr_6^{2-}$	0.882[i]	5.9×10^7 [l]	5.9×10^7	1.2×10^7 [d]	1.1×10^7 [e]
$Mo(CN)_8^{3-}$	0.80[h]	1.45×10^6 [l]	1.45×10^6	2.3×10^6 [d]	1.8×10^6 [e]
$CoW_{12}O_{40}^{5-}$	1.00[j]	2.4×10^5 [j]	2.4×10^5	1.6×10^6 [d]	1.5×10^6 [e]

[a] V. [b] L mol^{-1} s^{-1}; 20.0 °C. [c] Derived from eq 11, by assuming $k_{diff} = 5 \times 10^9$ L mol^{-1} s^{-1}. [d] Calculated with eq 9, by assuming $\lambda = 16$ kcal mol^{-1} for $Fe^{III}L_3$, $\lambda = 26$ kcal mol^{-1} for $IrCl_6^{2-}$, and so on, as reported in the text. $E°(HA\cdot/HA^-) = 0.88$ V. [e] Calculated with eq 9, by assuming λ's decreased by 2 kcal mol^{-1}; $E° = 0.93$ V. [f] Reference 52. [g] Reference 54. [h] Measured at $[HClO_4] = 1.0$ M, $\mu = 1$ M, 25 °C. [i] Reference 55. [j] Reference 34. [k] Reference 1. [l] This work. [m] The value for this complex is slightly anomalous. [n] Reference 55. [o] Reference 56. [p] Calculated with the same k_{diff} value, although ions with different charges are involved. [q] Calculated with $E°$ for $Fe(sphen)_3^{3+/2+}$ equal to 1.16 V (see ref 52).

and Z),[43] the comparison between calculated constants and observed ones is satisfactory.

Reactant Radii. According to the Marcus theory,[2] the parameter λ is equal to $\lambda_0 + \lambda_i$, where λ_0 is the solvent reorientation term and λ_i the contribution from the changes in bond lengths and angles in the molecules. If we tentatively neglect λ_i, then $\lambda = \lambda_0$ and

$$\lambda_0 = \left(\frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{r^*}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right)(\Delta ze)^2 \qquad (11)$$

where r_1 and r_2 are the radii of the reactants and D_{op} is the optical dielectric constant. The radius of ascorbate anion can be calculated by using eq 12, where r is the radius, ρ the

$$^4/_3\pi r^3 = M/N\rho \qquad (12)$$

density, M the molecular weight, and N Avogadro's number[45] (for ascorbic acid $r = 3.5$ Å).[46] By adopting the reported radii for complex ions,[47] the following values of λ's can be calculated: for Ir(IV) aquo complexes, $\lambda = 24.3$ kcal mol^{-1} (by assuming the same radius for the three complexes), for $Fe^{III}L_3$, $\lambda = 22.1$, and for $Mo(CN)_8^{3-}$, $\lambda = 23.4$. The comparison with the data previously reported shows a marked difference particularly for $Fe^{III}L_3$ and $Mo(CN)_8^{3-}$: probably water molecules are present in the activated complexes.

Conclusions

The investigation of the kinetic behavior of ascorbic acid toward different outer-sphere oxidizing agents (which exhibit different intrinsic parameters ΔG^{**}), allows an estimation of the reduction potentials of unstable species such as the radicals $H_2A^{+}\cdot$ and $HA\cdot$.

Moreover, it is noteworthy that in a homologous series of oxidizing agents (such as $Fe^{III}L_3$ or iridium(IV)–chloro complexes) the contribution of the acid-independent path, which is not relevant for the complexes with low reduction potentials, becomes the more important one for complexes with higher reduction potentials and that Marcus theory provides a reasonable explanation of these features.

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Registry No. Ascorbic acid, 50-81-7; $IrCl_6^{2-}$, 16918-91-5; $Ir(H_2O)Cl_5^-$, 19544-02-6; $Ir(H_2O)_2Cl_4$, 17348-35-5; $IrBr_6^{2-}$, 16919-98-5; $Mo(CN)_8^{3-}$, 17845-99-7; $Fe(phen)_2(CN)_2^+$, 28850-37-5; $Fe(bpy)_2(CN)_2^+$, 47597-23-9; $Fe(phen)(CN)_4^-$, 65749-14-6; $Fe(sphen)_3^{3+}$, 18955-00-5; $Fe(bphen)_3^{3+}$, 60502-69-4; $Fe(mphen)_3^{3+}$, 18024-61-8; $Fe(nphen)_3^{3+}$, 22327-24-8; $Fe(cphen)_3^{3+}$, 22327-23-7; $Fe(phen)_3^{3+}$, 13479-49-7; $Fe(dmphen)_3^{3+}$, 21924-26-5; $Fe(bpy)_3^{3+}$, 18661-69-3; $Fe(dmbpy)_3^{3+}$, 34032-03-6; $Fe(CN)_6^{3-}$, 13408-62-3; $CoW_{12}O_{40}^{5-}$, 12181-04-3.

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(19) This value leads to $\Delta G^{**} = 6.0$–7.0 kcal mol^{-1} for $H_2Q^{+}\cdot/H_2Q$ exchange, that is, the rate constant of 7×10^5–4×10^6 L mol^{-1} s^{-1} for the self-exchange rates. Since these values seem low with respect to other exchange rates between radicals and parent molecules,[14] it must be noted that the λ's for benzenediol oxidation were derived by setting the deprotonation constant of semiquinone of parent quinol ($H_2Q^{+}\cdot \rightleftharpoons HQ\cdot + H^+$) equal to 10 mol L^{-1}.[15b] If the effective value is higher, then $\Delta G°_{12}{}'$ is higher, and consequently the λ's which fit the data are lower. For example, by setting this deprotonation constant at 100 mol L^{-1}, the λ's are decreased by about 4 kcal mol^{-1}; then ΔG^{**} ($H_2Q^{+}\cdot/H_2Q$) = 4.0–5.0 kcal mol^{-1}; that is, self-exchange rate constants are 2×10^7–1×10^8 L mol^{-1} s^{-1}.

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Mechanism of the Reduction of Bromate Ion by Cyano(bipyridyl)iron(II) Complexes[1a]

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The kinetics of the $BrO_3{}^-$ oxidation of $Fe(bpy)(CN)_4{}^{2-}$, $Fe(bpy)_2(CN)_2$, and $Fe(bpy)_3{}^{2+}$ have been determined in acidic perchlorate solutions at 25.0 °C and 0.50 M ionic strength. Each reaction is autocatalytic, the first two complexes following the same mechanism as the $Fe(CN)_6{}^{4-}$ reaction, with the rate law $-d[Fe(II)]/dt = 6(c + d[H^+]^2)[Fe(II)][BrO_3{}^-] + 6k_3[Br^-][BrO_3{}^-][H^+]^2$ where $k_3 = 2.86$ M^{-3} s^{-1}, and $c = (6.2 \pm 1.1) \times 10^{-3}$ M^{-1} s^{-1}, $d = 0.227 \pm 0.018$ M^{-3} s^{-1} for $Fe(bpy)(CN)_4{}^{2-}$, and $c = (2.95 \pm 0.44) \times 10^{-2}$ M^{-1} s^{-1}, $d = 0.755 \pm 0.047$ M^{-3} s^{-1} for $Fe(bpy)_2(CN)_2$. A different rate law and mechanism were found for the autocatalytic $Fe(bpy)_3{}^{2+}$ reaction, with the slope ($-b$) of Guggenheim plots being given by $-b = g[BrO_3{}^-][H^+] + h[BrO_3{}^-]^2[H^+]^2$, where $g = 12.8 \pm 0.3$ M^{-2} s^{-1} and $h = 964 \pm 56$ M^{-4} s^{-1}. Rate correlations based on Marcus theory suggest that all these reactions proceed by outer-sphere mechanisms.

Introduction

One of the predictions of the Marcus theory for oxidation–reduction reactions[2,3] is that the relative rates of oxidation of a series of reducing agents by two different oxidants should be independent of the identity of the reducing agent if both sets of reactions are outer sphere. Comparison of the rates of the Cr(VI) oxidations[4] of $Fe(CN)_6{}^{4-}$, $Fe(bpy)(CN)_4{}^{2-}$ (bpy = 2,2′-bipyridyl), $Fe(bpy)_2(CN)_2$, and $Fe(bpy)_3{}^{2+}$ with the rates of the corresponding outer-sphere oxidations by Ce(IV)[5] suggested that the first three Fe(II) complexes reacted by an inner-sphere mechanism while the last system was outer sphere. These conclusions were supported by examination of the corresponding V(V) oxidations,[6,7] where the predictions of the relative rate comparisons were confirmed by observation of binuclear successor complexes with the cyanide-containing Fe(II) complexes. These rate comparisons thus appear to be