The Oxidation of Ascorbic Acid by Tris(2,2′-bipyridine) Complexes of Osmium(III), Ruthenium(III) and Nickel(III) in Aqueous Media: Applications of the Marcus Cross-Relation

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The kinetics of the outer-sphere oxidation of L-ascorbic acid (H_2A) by tris(2,2′-bipyridine) and tris(4,4′-dimethyl-2,2′-bipyridine) complexes of osmium(III), ruthenium(III), and nickel(III) have been investigated in acidic aqueous media at 9–25 °C. The observed inverse acid dependence, $-d[ML_3^{3+}]/dt = 2(k_1 + k_2K_1/[H^+])[ML_3^{3+}][H_2A]$, suggests a mechanism involving H_2A and HA^- pathways, for which the specific rate and activation parameters have been determined. These and previously reported rate constants for cross-reactions involving ascorbate species are correlated in terms of the Marcus relationships. Estimates of the self-exchange parameters for the one-electron couples: $H_2A/H_2A^{\dot{+}}$, $k_{11} = 2 \times 10^3$ M^{-1} s^{-1}; $HA^-/HA\cdot$, $k_{11} = 1 \times 10^5$ M^{-1} s^{-1}; $A^{2-}/A^{\dot{-}}$, $k_{11} = 2 \times 10^5$ M^{-1} s^{-1}, based on ascorbate radical reduction potentials calculated from proton and redox equilibrium constants, are presented.

Introduction

Ascorbic acid is widely used as a reducing agent in chemical and biological systems [1–9] and is finding increasing application as a reductant in photoconversion schemes [5]. Consequently knowledge of the kinetic parameters that characterize the rates of ascorbate reductions is highly desirable. Although several studies addressing this question have recently been published [2, 7, 10], there is still some uncertainty concerning the kinetic parameters for the elementary steps. Depending on the nature of the oxidant and the acidity of the reaction medium, either the undissociated ascorbic acid (H_2A), the ascorbate anion (HA^-), or the ascorbate dianion (A^{2-}) is the kinetically important ascorbate species. Pelizzetti and co-workers [2] have estimated the $H_2A^{\dot{+}}/H_2A$ and $HA\cdot/HA^-$ reduction potentials to be 1.35 and 0.93 V, respectively, by assuming large self-exchange rate constants (10^6–10^8 M^{-1} s^{-1}) for the ascorbate couple. Creutz [10] has recently re-examined the thermodynamic data available for the ascorbate system and suggested a value of 0.70 V for the $HA\cdot/HA^-$ couple. This lower reduction potential implicated a lower self-exchange rate constant for the ascorbate/ascorbate radical couple. More recently, Williams and Yandell [7] have reported rate constants for the oxidation of HA^- and A^{2-} which are consistent with the latter E^0 value but with a self-exchange rate constant of 10^6 M^{-1} s^{-1} for both the $HA^-/HA\cdot$ and $A^{2-}/A^{\dot{-}}$ couples.

In the present paper we report the results of a kinetic study of the oxidation of ascorbic acid by the tris(2,2′-bipyridine) and tris(4,4′-dimethyl-2,2′-bipyridine) complexes of osmium(III), ruthenium(III), and nickel(III) in acidic aqueous media. By the use of these strong outer-sphere oxidants, whose self-exchange rate constants and electrochemical parameters are known, we have extended the range of available kinetic data and have been able to further characterize the $H_2A/H_2A^{\dot{+}}$ couple. A modified Marcus relationship has been utilized to correlate the cross-reaction data from this work and rate constants for the quenching of the metal-to-ligand charge-transfer excited state of RuL_3^{2+} (L is a substituted bipyridine or phenanthroline) and other recent data in the literature to provide an estimate of the self-exchange rate constants for the ascorbate/ascorbate radical couples, $H_2A/H_2A^{\dot{+}}$, $HA^-/HA\cdot$, and $A^{2-}/A^{\dot{-}}$.

Experimental

Materials

Trifluoromethanesulfonic acid (CF_3SO_3H, 3M Co.) was distilled twice under reduced pressure. Lithium trifluoromethanesulfonate was prepared by neutralization of the distilled CF_3SO_3H with recrystallized Li_2CO_3. For the determination of the concentration of stock CF_3SO_3Li solutions, an aliquot was passed through a Dowex 50W-X8 column in the H^+ form and titrated with standardized NaOH. L-Ascorbic acid (Fisher) was used without further purification.

The tris(2,2′-bipyridine) and tris(4,4′-dimethyl-2,2′-bipyridine) complexes of osmium(II) and ruthenium(II) were prepared as described previously [12, 13]. The Os(III) and Ru(III) complexes were made by oxidation of the divalent species with lead(IV) dioxide in dilute sulfuric acid. The perchlorate salts were isolated by addition of excess sodium perchlorate to the filtered solutions.

The perchlorate salts of $Ni(bpy)_3^{2+}$ and $Ni(dmbpy)_3^{2+}$ were prepared by the addition of a slight stoichiometric excess of the ligand (G. F. Smith) to a solution of nickel perchlorate in methanol. The precipitated solid was washed with ethanol and ether and dried under vacuum. The nickel(III) salts were synthesized electrochemically in anhydrous acetonitrile containing 0.1 *M* tetraethylammonium perchlorate [14]. The acetonitrile was dried and distilled over CaH_2 under argon. The dark green nickel(III) complexes were obtained by slow evaporation of the solvent to near dryness. The solid was filtered, washed with a minimum of ice-cooled CH_3CN and stored in a dessicator at 0 °C.

Kinetic Measurements

The kinetics of the oxidation of ascorbic acid were studied by use of a Durrum D-110 stopped-flow spectrophotometer. The reactions were monitored at 400 nm for the nickel complexes and at 460–480 nm for the ruthenium and osmium complexes. Pseudo-first-order conditions of an excess of ascorbic acid over metal oxidant concentrations were employed. The acid concentration was varied between 0.01 and 1.00 *M* (CF_3SO_3H) with the ionic strength maintained at 1.00 *M* by the addition of CF_3SO_3Li. Solutions containing ascorbic acid were prepared immediately prior to use. The kinetic measurements were performed at three temperatures between 9° and 25 °C with thermostating (±0.1 °C) provided by an external water bath.

Electrochemical Measurements

The reduction potentials of the metal complexes used in this study were determined by means of cyclic voltammetry measurements. A PAR Model 175 potentiostat and Model 173 universal programmer were used along with a Hewlett-Packard x-y recorder. A three-compartment cell containing glassy-carbon working, platinum counter, and saturated calomel reference electrodes was employed. The reduction potentials were determined in 1.0 *M* CF_3SO_3H with metal complex concentrations of $(0.5–2.0) \times 10^{-3}$ *M*.

Results

The stoichiometry of the reactions between L-ascorbic acid and the metal complexes used in this study were determined by spectrophotometric titrations of the metal oxidants with ascorbic acid in 1.0 *M* CF_3SO_3H. For the OsL_3^{3+} and RuL_3^{3+} complexes the titrations were monitored at the visible maxima of the ML_3^{2+} species [12, 13], while for the NiL_3^{3+} complexes the changes in Ni(III) concentration were determined using $Fe(phen)_3^{2+}$. The ratio of mols of oxidant consumed per mol of ascorbic acid added was found to be (2.0 ± 0.1):1.0, suggesting the overall stoichiometry shown in eqn. 1

$$2ML_3^{3+} + H_2A \longrightarrow 2ML_3^{2+} + A + 2H^+ \tag{1}$$

where A is dehydroascorbic acid.

Kinetic Studies

The reactions between ascorbic acid and the metal complexes were carried out under pseudo-first-order conditions with the reductant concentration in excess. Plots of $\ln(A_\infty - A_t)$ or $\ln(A_t - A_\infty)$ against time were found to be linear for at least three half-lives. The pseudo-first-order rate constants exhibited a linear dependence on ascorbic acid concentration.

The second-order rate constants k_{obsd} increase with decreasing acidity. The nickel and ruthenium complexes were studied in the range $[H^+] = 0.2–1.0$ *M* (Fig. 1) and the osmium complexes in the range $[H^+] = 0.01–1.00$ *M* (Fig. 2). The plots of k_{obsd} against $1/[H^+]$ are linear for each of the oxidants with positive intercepts. From the observed inverse acid dependence and reaction stoichiometry the rate law may be expressed as

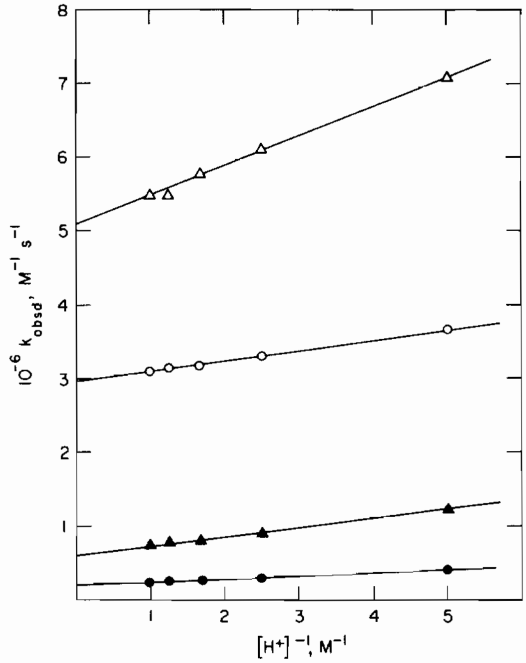


Fig. 1. Plots of second-order rate constants k_{obsd} against $[H^+]^{-1}$ at 25 °C, $\mu = 1.00$ *M* (CF_3SO_3Li). $Ru(dmbpy)_3^{3+}$ ●, $Ni(dmbpy)_3^{3+}$ ▲, $Ru(bpy)_3^{3+}$ ○, and $Ni(bpy)_3^{3+}$ △.

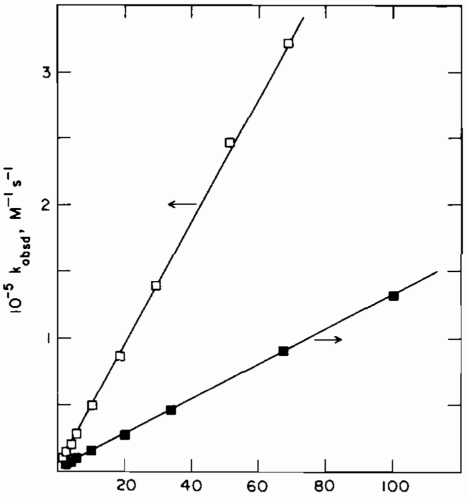


Fig. 2. Plots of second-order rate constants k_{obsd} against $[H^+]^{-1}$ at 25 °C, $\mu = 1.00$ *M* (CF_3SO_3Li). $Os(dmbpy)_3^{3+}$ ■ (right hand ordinate), $Os(bpy)_3^{3+}$ □ (left hand ordinate).

$$-\frac{d[ML_3^{3+}]}{2dt} = k_{obsd}[ML_3^{3+}][H_2A] \qquad (2)$$

where $k_{obsd} = k_a + k_b/[H^+]$.

The $1/[H^+]$ dependence was studied at three temperatures for each oxidant and the rate constants and activation parameters determined for the acid-dependent and acid-independent pathways are presented in Table I.

Cyclic Voltammetry

The reduction potentials of the $M(bpy)_3^{3+}$ and $M(dmbpy)_3^{3+}$ complexes in 1.0 *M* CF_3SO_3H were determined by cyclic voltammetry measurements. The electrode process exhibited reversible behavior for each complex, with peak separations of 60–70 mV at scan rates of 20–100 mV s^{-1}. The reduction potentials (*vs.* NHE) are reported in Table II. The potentials for $Ni(dmbpy)_3^{3+/2+}$ and $Ni(bpy)_3^{3+/2+}$ are in good agreement with the values obtained previously from an extrapolation of the potentials measured in acetonitrile solution [14, 15]. For the osmium and ruthenium complexes, the reduction potentials are similar to the values found in 1.0 *M* H_2SO_4 [13, 16].

Discussion

The metal complexes used in this study are outer-sphere one-electron oxidants and the sequence of two one-electron transfers would be expected in the

TABLE I. Rate Constants and Activation Parameters for the Oxidation of $H_2A(k_1)$ and $HA^-(k_2)$ by ML_3^{3+} Complexes, $\mu = 1.00$ *M* (CF_3SO_3H/Li^+).

Oxidant	T, °C	k_1, M^{-1} s^{-1}	$\Delta H_1^{\ddagger a}$	$\Delta S_1^{\ddagger b}$	k_2,^{c} M^{-1} s^{-1}	$\Delta H_2^{\ddagger a,d}$	$\Delta S_2^{\ddagger b,d}$
$Os(dmbpy)_3^{3+}$	9.7	⩽2			6.03×10^5	6.7	−8
	18.5	⩽4			8.31×10^5		
	25.0	⩽6			1.18×10^6		
$Os(bpy)_3^{3+}$	9.5	2.35×10^3	5.7	−23	3.15×10^7	2.5	−15
	18.3	3.15×10^3			3.61×10^7		
	25.0	4.22×10^3			4.21×10^7		
$Ru(dmbpy)_3^{3+}$	10.4	1.24×10^5	2.7	−25	$3.56(3.87) \times 10^8$	(1.8)	(−13)
	18.2	1.48×10^5			$3.97(4.35) \times 10^8$		
	25.0	1.66×10^5			$4.35(4.80) \times 10^8$		
$Ru(bpy)_3^{3+}$	10.0	2.48×10^6	1.4	−24	$1.34(1.93) \times 10^9$	(−1.9)	(−23)
	18.7	2.71×10^6			$1.28(1.79) \times 10^9$		
	25.0	2.96×10^6			$1.24(1.70) \times 10^9$		
$Ni(dmbpy)_3^{3+}$	9.9	5.31×10^5	0.7	−30	$1.07(1.41) \times 10^9$	(2.3)	(−8)
	18.5	5.52×10^5			$1.25(1.73) \times 10^9$		
	25.0	5.98×10^5			$1.30(1.81) \times 10^9$		
$Ni(bpy)_3^{3+}$	10.0	4.4×10^6	0.9	−25	$4.4(\geqslant 100) \times 10^9$		
	18.6	4.7×10^6			$4.2(60) \times 10^9$		
	25.0	5.1×10^6			$3.8(20) \times 10^9$		

[a] Uncertainty is ±1.0 kcal mol^{-1}. [b] Uncertainty is ±4 cal deg^{-1} mol^{-1}. [c] Observed k_2 rate constants. Values in parenthesis are $k_{2,act}$: these are the k_2 values corrected for diffusion using eqn. 9 with $k_{diff}(T) = 4.4 \times 10^9$ (10 °C), 4.5×10^9 (18 °C), and 4.6×10^9 M^{-1} s^{-1} (25 °C). [d] Activation parameters in parenthesis calculated using $k_{2,act}$ values.

TABLE II. Proton Equilibrium Constants and Reduction Potentials for the Ascorbic Acid System at 25 °C. Ionic Strengths Given in Parentheses.

Equilibrium	pK
$H_2A \rightleftharpoons HA^- + H^+$	$pK_1 = 3.95\ (1.0)$[a]
$HA^- \rightleftharpoons A^{2-} + H^+$	$pK_2 = 11.24 \pm 0.02\ (1.0)$[b]
$H_2A^{\overset{+}{\cdot}} \rightleftharpoons HA\cdot + H^+$	$pKr_1 = -4 \pm 1$[c]
$HA\cdot \rightleftharpoons A^{\overset{-}{\cdot}} + H^+$	$pKr_2 = -0.45 \pm 0.10$[d]
Couple	**E^0, V (*vs.* NHE)**
$H_2A^{\overset{+}{\cdot}} + e^- \longrightarrow H_2A$	$E_1^0 = +1.17 \pm 0.06$[e]
$HA\cdot + e^- \longrightarrow HA^-$	$E_2^0 = +0.71 \pm 0.01$[f]
$A^{\overset{-}{\cdot}} + e^- \longrightarrow A^{2-}$	$E_3^0 = +0.015 \pm 0.005$[g]

[a] Ref. 8. [b] Ref. 3. [c] Estimated as described in text. [d] Ref. 17, ionic strength not defined. [e] Calculated using eqn. 16. [f] Calculated using eqn. 15. [g] Ref. 22.

oxidation of ascorbic acid to dehydroascorbic acid. The inverse dependence of the observed rate constants on $[H^+]$ at low pH, observed previously with other metal oxidants [1–4, 8, 9], is consistent with the rate-determining pathways (eqns. 3–5) involving the undissociated ascorbic acid and the ascorbate anion ($pK_1 = 3.96$ [8]).

$$H_2A \overset{K_1}{\rightleftharpoons} HA^- + H^+ \tag{3}$$

$$ML_3^{3+} + H_2A \xrightarrow{k_1} ML_3^{2+} + H_2A^{\overset{+}{\cdot}} \tag{4}$$

$$ML_3^{3+} + HA^- \xrightarrow{k_2} ML_3^{2+} + HA\cdot \tag{5}$$

The ascorbate radical intermediates are strong acids [17] ($pKr_2(HA\cdot) = -0.45$) such that deprotonation leaves $A^{\overset{-}{\cdot}}$ as the predominant radical species in solution at pH > 0. The ascorbate radical anion likely disappears rapidly as a result of oxidation by ML_3^{3+} (eqn. 6) and/or through a disproportionation reaction (eqn. 7).

$$ML_3^{3+} + A^{\overset{-}{\cdot}} \xrightarrow{\text{fast}} ML_3^{2+} + A \tag{6}$$

$$A^{\overset{-}{\cdot}} + A^{\overset{-}{\cdot}} \xrightarrow{H^+} H_2A + A \tag{7}$$

Despite the rather large self-exchange barrier proposed [10] for the $A^{\overset{-}{\cdot}}/A$ couple ($k_{11} \leq 10^{-1}\ M^{-1}\ s^{-1}$) the substantial thermodynamic driving force (for $A + e^- \rightleftharpoons A^{\overset{-}{\cdot}}$, $E^0 = -0.14$ V [10]) could make the oxidation of $A^{\overset{-}{\cdot}}$ by strong oxidants such as the ML_3^{3+} species a diffusion-controlled process. The rate constant for $A^{\overset{-}{\cdot}}$ disproportionation in the acidity range $[H^+] = 0.1–1.0\ M$ has been estimated to be $\geq 10^8\ M^{-1}\ s^{-1}$ [18].

On the basis of this mechanism on expression for k_{obsd} (eqn. 2) may be written in the form

$$k_{obsd} = \frac{k_1 + k_2K_1/[H^+]}{1 + K_1/[H^+]} \tag{8}$$

where $k_a = k_1$ and $k_b = k_2K_1$ when $K_1 \ll [H^+]$. The rate constants k_1 and k_2 for each of the oxidants at three temperatures are presented in Table I. The dissociation constant K_1 has been measured at several temperatures in 1.0 *M* ionic strength media [4, 8] and the values used in the determination of k_2 were interpolated from these reported values. The rate constants for the reactions of the ruthenium(III) and nickel(III) complexes with HA^- are very large and approach the limit of diffusion-controlled processes. The contribution of diffusion to the observed value of k_2 may be eliminated using eqn. 9

$$\frac{1}{k_{act}} = \frac{1}{k_{obsd}} - \frac{1}{k_{diff}} \tag{9}$$

where k_{diff} is the diffusion-controlled rate constant and k_{act} is the activation-controlled rate constant [19]. For the reaction of a +3 and a −1 ion forming an activated complex of radius ~10 Å, a value of $k_{diff} \sim 4.6 \times 10^9\ M^{-1}\ s^{-1}$ is estimated at 25 °C. The k_2 values corrected for diffusion using eqn. 9 are reported in Table I.

The activation parameters corresponding to the individual pathways are also presented in Table I. The small enthalpies and large negative entropies associated with the oxidation of H_2A and HA^- by the metal complexes in this study have been observed previously by Pelizzetti and co-workers for similar oxidants [1, 2]. Slightly negative ΔH^+ values, found here for the oxidation of HA^- by $Ru(bpy)_3^{3+}$, have also been reported [2] for the oxidation of HA^- by $Ir(H_2O)Cl_5^-$ and $Mo(CN)_8^{3-}$.

The ratio of k_2/k_1 is approximately 10^4 for each oxidant listed in Table I. The difference in the reactivities of H_2A and HA^- towards a given oxidant and the variations in k_1 and k_2 with the nature of the oxidant may be rationalized in terms of the reduction potentials and self-exchange parameters of the redox couples, as described by the Marcus theory [11]. In terms of a recent modification of the theory [20], the rate constant for a cross-reaction k_{12} is related to the rate constants for the component exchange reactions k_{11} and k_{22} and the equilibrium constant for the cross reaction K_{12} by

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12} \tag{10}$$

where

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4\left[\ln\left(\frac{k_{11}k_{22}}{A_{11}A_{22}}\right) + \frac{w_{11} + w_{22}}{RT}\right]} \tag{11}$$

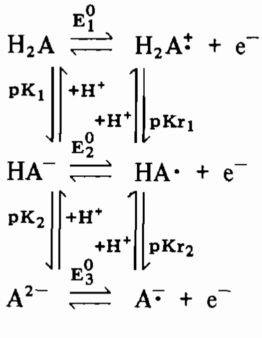
$$W_{12} = \exp[-(w_{12} + w_{21} - w_{11} - w_{22})/2RT] \qquad (12)$$

$$w_{ij} = \frac{z_i z_j e^2}{D_s \sigma_{ij}(1 + \beta\sigma_{ij}\sqrt{\mu})} \qquad (13)$$

$$A_{ii} = \left[\frac{4\pi N\sigma^2 \nu_n \delta r}{1000}\right]_{ii} \qquad (14)$$

In these expressions w_{ij} is the work required to bring ions i and j (charges z_i and z_j) to the separation distance σ_{ij} (taken equal to the sum of a_i and a_j, the radii of ions i and j) [21], $\beta = (8\pi Ne^2/1000D_skT)^{1/2}$, ν_n is the nuclear vibration frequency that destroys the activated complex configuration, and δr is the thickness of the reaction layer. The value of A/σ^2 ranges from 10^{10}–10^{11} M^{-1} Å^{-2} s^{-1}, the exact value depending on the particular reaction: a typical value is 3×10^{10} M^{-1} Å^{-2} s^{-1} and this value will be used here.

The above equations are useful for estimating unknown self-exchange rate constants and redox potentials from experimental kinetic and thermodynamic data for a series of cross reactions with reactants for which these intrinsic parameters are known. The ascorbate/ascorbate radical system is somewhat complicated by the proton equilibria associated with both the oxidized and reduced forms. The relevant proton and redox equilibria are presented in the following scheme.



Scheme 1

The potential of the $A^{\dot{-}}/A^{2-}$ couple E_3^0 has been measured by Steenken and Neta [22] at pH 13.5 and found to be 0.015 V. The $HA\cdot/HA^-$ potential E_2^0 may be calculated (eqn. 15) using this value of E_3^0 and the proton equilibrium constants K_2 ($pK_2 = 11.24$, $\mu = 1.0$ *M*) [3] and Kr_2 ($pKr_2 = -0.45$) [17].

$$E_2^0 = E_3^0 + 0.059\,(pK_2 - pKr_2) \qquad (15)$$

The potential obtained in this manner is +0.71 V, in good agreement with the values estimated by Creutz [10] (+0.70 V, $\mu = 0.1$ *M*) and Williams and Yandell [7] (+0.723 V, $\mu = 0.1$ *M*). A calculation of the $H_2A^{\dot{+}}/H_2A$ reduction potential E_1^0 (eqn. 16)

$$E_1^0 = E_3^0 + 0.059\,(pK_1 + pK_2 - pKr_1 - pKr_2) \qquad (16)$$

TABLE III. Rate Constants for the Oxidation of Ascorbic Acid (k_1), the Ascorbate Anion (k_2), and the Ascorbate Dianion (k_3). Ionic Strength Given in Parentheses.

Oxidant[a]	E^0, V	k_{22}, M^{-1} s^{-1}	a, Å[b]	k_1, M^{-1} s^{-1}	k_2, M^{-1} s^{-1}	k_3, M^{-1} s^{-1}
$Ni(bpy)_3^{3+}$ [c]	1.72	$2 \times 10^3(1.0)$[d]	6.8	$5.1 \times 10^6(1.0)$	$2.2 \times 10^{10}(1.0)$	
$Ru(bpy)_3^{3+}$[c]	1.26	$4 \times 10^8(0.1)$[e]	6.8	$3.0 \times 10^6(1.0)$	$1.7 \times 10^9(1.0)$	
$Fe(phen)_3^{3+}$	1.06	$3 \times 10^8(5.5)$[f]	6.8	$3.0 \times 10^4(1.0)$[g] $1.7 \times 10^5(1.0)$[h]	$2.0 \times 10^9(1.0)$[g] $6.5 \times 10^8(1.0)$[h]	
$CoW_{12}O_{40}^{5-}$[i]	1.00	1.7(1.0)[j]	5.0	77.4(1.0)	$2.4 \times 10^5(1.0)$	
$Ni(cyclam)^{3+}$[k]	0.95	$1 \times 10^3(1.0)$[l]	5.0	$2.5 \times 10^2(1.0)$	$1.1 \times 10^6(1.0)$	
$Os(bpy)_3^{3+}$ [c]	0.81	$4 \times 10^8(0.1)$[e]	6.8	$4.2 \times 10^3(1.0)$	$4.2 \times 10^7(1.0)$	
$*Ru(phen)_3^{3+}$ [m]	0.77	$\sim 10^9(0.7)$	6.8		$2.3 \times 10^8(0.7)$	
$Fe(CN)_5tu^{2-}$ [n]	0.35	$1 \times 10^5(1.0)$[o]	5.0		66(1.0)	$8.8 \times 10^7(1.0)$
$Co(bpy)_3^{3+}$ [p]	0.32	18(0.1)[q]	6.8		0.13(0.1)	$2.1 \times 10^6(0.1)$
$Ru(NH_3)_5py^{3+}$ [o]	0.32	$1.1 \times 10^5(0.1)$[r]	3.8			$6.0 \times 10^9(0.1)$[s]

[a] Ligand abbreviations: bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, tpy = 2,2′:6′,2″-terpyridine, dmbpy = 4,4′-dimethyl-2,2′-bipyridine, mphen = 5-methyl-1,10-phenanthroline, dmphen = 4,7-dimethyl-1,10-phenanthroline, 5,6-dmphen = 5,6-dimethyl-1,10-phenanthroline, cphen = 5-chloro-1,10-phenanthroline, bphen = 5-bromo-1,10-phenanthroline, nphen = 5-nitro-1,10-phenanthroline, sphen = 1,10-phenanthroline-5-sulfonic acid, 3,5,6,8-tmphen = 3,5,6,8-tetramethyl-1,10-phenanthroline, 3,4,7,8-tmphen = 3,4,7,8-tetramethyl-1,10-phenathroline, py = pyridine, tu = thiourea, dipic = pyridine-2,6-dicarboxylate, cyclam = 1,4,8,11-tetraazacyclotetradecane, tet-*a* = meso-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, tet-*c* = meso-5,5,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane. [b] The radius *a* is calculated using $a = 1/2(d_1d_2d_3)^{1/3}$ where d_i is the diameter of the ion along a given axis [27]. [c] This work. [d] Ref. 26. [e] Ref. 25. [f] Ref. 24. [g] Ref. 2. [h] Ref. 8. [i] Ref. 4. [j] D. G. Rasmussen and C. H. Brubaker, *Inorg. Chem., 3,* 977 (1964). [k] Ref. 9. [l] A. McAuley, D. H. Macartney and T. Oswald, *J. Chem. Soc., Chem. Comm.,* 274 (1982). [m] Ref. 5. [n] Ref. 3. [o] Ref. 7. [p] Ref. 6. [q] H. M. Neumann, quoted in R. Farina and R. G. Wilkins, *Inorg. Chem., 7,* 516 (1968). [r] Ref. 27. [s] Not corrected for diffusion.

requires a knowledge of the acid dissociation constant Kr_1 for the ascorbate cation radical. This constant has not been determined experimentally but may be estimated from a comparison of the proton equilibria data for similar compounds such as hydroquinone and other benzene diols [23]. The spread of pK values in these complexes and their relationship to the corresponding redox potentials suggest a value of $pKr_1 = -4 \pm 1$ for the ascorbic acid system. This estimate corresponds (eqn. 16) to a reduction potential of 1.17 ± 0.06 V for $H_2A^{\dot{+}}/H_2A$. The various measured and estimated proton equilibrium constants and one-electron reduction potentials for the ascorbic acid system are presented in Table II.

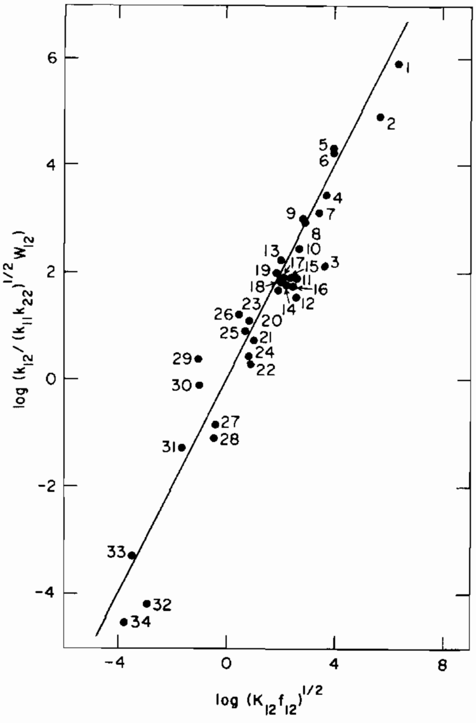


Fig. 3. Logarithm of $(k_{12}/(k_{11}k_{22})^{1/2}W_{12})$ *vs.* the logarithm of $(K_{12}f_{12})^{1/2}$ for the oxidation of the ascorbate monoanion by [27]: 1. $Ni(bpy)_3^{3+}$ (this work); 2. $Ni(dmbpy)_3^{3+}$ (this work); 3. $Ru(bpy)_3^{3+}$ (this work); 4. $Fe(nphen)_3^{3+}$ (ref. 1); 5. $Ni(tet\text{-}a)^{3+}$ (ref. 9); 6. $Ni(tet\text{-}c)^{3+}$ (ref. 9); 7. $Fe(sphen)_3^{3+}$ (ref. 2); 8. $Fe(bphen)_3^{3+}$ (ref. 2); 9. $Fe(cphen)_3^{3+}$ (ref. 1); 10. $Fe(phen)_3^{3+}$ (ref. 1); 11. $Fe(phen)_3^{3+}$ (ref. 8); 12. $Ru(dmbpy)_3^{3+}$ (this work); 13. $Fe(mphen)_3^{3+}$ (ref. 1); 14. $Fe(bpy)_3^{3+}$ (ref. 2); 15. $CoW_{12}O_{40}^{5-}$ (ref. 4); 16. $*Ru(bphen)_3^{2+}$ (ref. 5); 17. $*Ru(cphen)_3^{2+}$ (ref. 5); 18. $Fe(dmphen)_3^{3+}$ (ref. 1); 19. $IrCl_6^{2-}$ (ref. 2); 20. $Ni(cyclam)^{3+}$ (ref. 9); 21. $Fe(dmbpy)_3^{3+}$ (ref. 2); 22. $*Ru(bpy)_3^{2+}$ (ref. 5); 23. $*Ru(mphen)_3^{2+}$ (ref. 5); 24. $Os(bpy)_3^{3+}$ (this work); 25. $*Ru(5,6\text{-}dmphen)_3^{2+}$ (ref. 5); 26. $*Ru(phen)_3^{2+}$ (ref. 5); 27. $*Ru(dmbpy)_3^{2+}$ (ref. 5); 28. $Os(dmbpy)_3^{3+}$ (this work); 29. $*Ru(3,5,6,8\text{-}tmphen)_3^{2+}$ (ref. 5); 30. $*Ru(3,4,7,8\text{-}tmphen)_3^{2+}$ (ref. 5); 31. $Ru(NH_3)_4bpy^{3+}$ (ref. 7); 32. $Co(phen)_3^{3+}$ (ref. 6); 33. $Fe(CN)_5tu^{2-}$ (ref. 3); 34. $Co(bpy)_3^{3+}$ (ref. 6). Points calculated using $k_{11}(HA^-/HA\cdot)$ $= 1 \times 10^5$ M^{-1} s^{-1}. Solid line represents the theoretical slope of unity.

The tris(bipyridine) complexes of the iron triad have been well studied. The self-exchange rate constants for the $FeL_3^{2+/3+}$ ($k_{22} = 3 \times 10^8$ M^{-1} s^{-1}, $\mu = 5.5$ M) [24] and $RuL_3^{2+/3+}$ ($k_{22} = 4 \times 10^8$ M^{-1} s^{-1}, $\mu = 0.10$ M) [25] couples have been measured and the $OsL_3^{2+/3+}$ rate constant is assumed to be very similar. The $NiL_3^{2+/3+}$ self-exchange rate constant is much slower, with a value of 2×10^3 M^{-1} s^{-1} ($\mu = 1.0$ M) estimated recently from cross-reaction kinetic studies involving NiL_3^{3+} and several reductants [26]. The similarity in the cross-reaction rate constants for the ascorbic acid oxidations by RuL_3^{3+} and NiL_3^{3+}, despite the large difference in their reduction potentials, may be therefore attributed to the differences in the self-exchange parameters.

The Marcus relationship (eqn. 10) may be used to calculate k_{11} values for the $H_2A/H_2A^{\dot{+}}$, $HA^-/HA\cdot$, and $A^{2-}/A^{\dot{-}}$ couples from the cross-reaction data available from this study and the literature. Table III presents the relevant kinetic and electrochemical data for several complexes which are representative of the oxidants employed in the kinetic studies. Using eqns. 10–14, an estimate of the best value of k_{11} for each ascorbate/ascorbate radical couple was made using the cross-reaction data for the particular couple. The values were incorporated into plots of $\log(k_{12}/(k_{11}k_{22})^{1/2}W_{12})$ against $\log(K_{12}f_{12})^{1/2}$, shown in Figs. 3, 4 and 5 for the $H_2A/H_2A^{\dot{+}}$, $HA^-/HA\cdot$, and $A^{2-}/A^{\dot{-}}$ couples, respectively. Equation 10 predicts a slope of unity for this relationship, as depicted by the solid line in these figures.

For the $HA^-/HA\cdot$ couple, for which a substantial body of data (including the reactions of ascorbate with both ground- and excited-state metal complexes) is available, a k_{11} value of 1×10^5 M^{-1} s^{-1} is obtained in the present analysis. Excellent adherence to the theoretical slope is observed, especially when $\log(K_{12}f_{12})^{1/2}$, a function of the thermodynamic driving force, is not far from zero. In the reactions involving CoL_3^{3+} and NiL_3^{3+} (L = phen or bpy), the larger magnitude of $\log(K_{12}f_{12})^{1/2}$ is accompanied by deviations from the theoretical slope. This phenomenon has been noted previously for cross-reactions with large thermodynamic driving forces [29]. The estimated k_{11} value is in reasonable agreement with $k_{11} = 10^6$ M^{-1} s^{-1} obtained by Williams and Yandell [7] from a smaller set of data and a different form of the Marcus equation.

For the $H_2A/H_2A^{\dot{+}}$ couple a self-exchange rate constant of 2×10^3 M^{-1} s^{-1} was estimated. Excellent agreement with the theoretical slope is again observed (Fig. 4) over a wide range of the thermodynamic driving forces. The uncertainty of one pK unit in the value estimated for pKr_1 and the resultant 0.06 V in

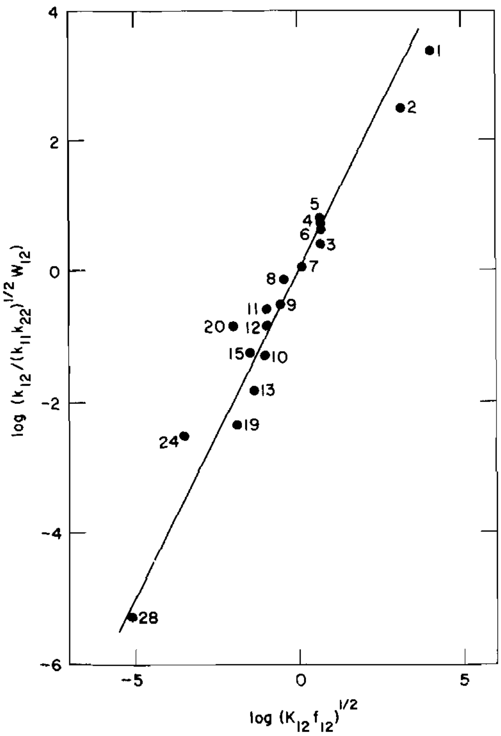


Fig. 4. Logarithm of $(k_{12}/(k_{11}k_{22})^{1/2}W_{12})$ *vs.* the logarithm of $(K_{12}f_{12})^{1/2}$ for the oxidation of ascorbic acid. Points are calculated using $k_{11}(H_2A/H_2A^{\overset{+}{\cdot}}) = 2 \times 10^3\ M^{-1}\ s^{-1}$ and numbered according to the legend in Fig. 3. Solid line represents the theoretical slope of unity.

E_1^0 correspond to an order of magnitude uncertainty in the self-exchange rate constant for the $H_2A/H_2A^{\overset{+}{\cdot}}$ couple. Using 1.23 V for the reduction potential of $H_2A^{\overset{+}{\cdot}}$, for example, would require a value of $k_{11} = 2 \times 10^4\ M^{-1}\ s^{-1}$ to satisfy eqn. 10. The reduction potential and self-exchange rate constant estimated for $H_2A^{\overset{+}{\cdot}}/H_2A$ are lower than the values estimated by Pelizzetti and co-workers [2]. In view of their overestimation of the corresponding $HA\cdot/HA^-$ exchange parameters the present values for the $H_2A^{\overset{+}{\cdot}}/H_2A$ couple are considered more reliable, pending a more definite value of pKr_1.

Kinetic data for the oxidation of the ascorbate dianion are somewhat limited at present. From the available cross-reaction parameters a self-exchange rate constant of $2 \times 10^5\ M^{-1}\ s^{-1}$ for the $A^{2-}/A^{\overline{\cdot}}$ couple was estimated and a reasonable correlation is seen in the plot in Fig. 5. Within the uncertainties inherent in the Marcus equations, this value of k_{11} is in good agreement with the values, $\sim 10^5$ and $10^6\ M^{-1}\ s^{-1}$, estimated by Creutz [10] and Williams and Yandell [7], respectively. Further kinetic studies of the reactions of A^{2-} with outer-sphere oxidants possessing reduction potentials <0.30 V would be of use in the refinement of the current self-exchange estimates.

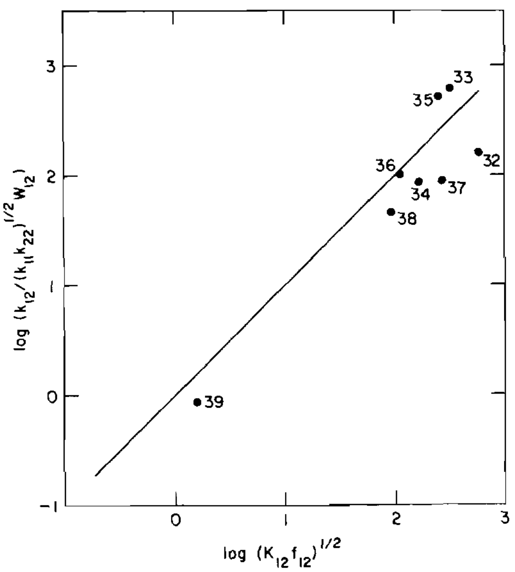


Fig. 5. Logarithm of $(k_{12}/(k_{11}k_{22})^{1/2}W_{12})$ *vs.* the logarithm of $(K_{12}f_{12})^{1/2}$ for the oxidation of the ascorbate dianion by: 32. $Co(phen)_3^{3+}$ (ref. 6); 33. $Fe(CN)_5tu^{2-}$ (ref. 3); 34. $Co(bpy)_3^{3+}$ (ref. 6); 35. $Ru(NH_3)_5py^{3+}$ (ref. 7); 36. $Co(tpy)_2^{3+}$ (ref. 7); 37. $Ru(dipic)_2^-$ (ref. 7); 38. cytochrome c (ref. 28); 39. catechol anion radical (ref. 22). Points are calculated using $k_{11}(A^{2-}/A^{\overline{\cdot}}) = 2 \times 10^5\ M^{-1}\ s^{-1}$. Solid line represents the theoretical slope of unity.

Conclusions

The cross-relation, eqn. 10, successfully correlates a wide variety of reductions by ascorbic acid (Fig. 4), the ascorbate monoanion (Fig. 3), and the ascorbate dianion (Fig. 5). The agreement with the cross-relation is particularly gratifying for the reductions by the ascorbate monoanion: this data set is the most extensive and the rate constants span 10 orders of magnitude. The ascorbate/ascorbate radical self-exchange rate constants increase in the order: $H_2A/H_2A^{\overset{+}{\cdot}} < HA^-/HA\cdot \leqslant A^{2-}/A^{\overline{\cdot}}$. The small dependence of k_{11} on the extent of protonation in these species likely results from the effects of protonation on the inner-sphere reorganization barriers [10]. Structural characterization of the various ascorbate and ascorbate radical species would be of considerable value in the further evaluation of these effects.

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References

1 E. Pelizzetti, E. Mentasti and E. Pramauro, *Inorg. Chem.*, *15* 2898 (1976).
2 E. Pelizzetti, E. Mentasti and E. Pramauro, *Inorg. Chem.*, *17*, 1181 (1978).
3 D. H. Macartney and A. McAuley, *Can. J. Chem.*, *59*, 132 (1981).
4 Z. Amjad, J. C. Brodovitch and A. McAuley, *Can. J. Chem.*, *55*, 3581 (1977).
5 C. V. Krishnan, C. Creutz, D. Mahajan, H. Schwarz and N. Sutin, *Isr. J. Chem.*, *22*, 98 (1982).
6 K. Tsukahara and Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, *54*, 2642 (1981).
7 N. H. Williams and J. K. Yandell, *Aust. J. Chem.*, *35*, 1133 (1982).
8 M. Kimura, M. Yamamoto and S. Yamabe, *J. Chem. Soc., Dalton Trans.*, 423 (1982).
9 A. McAuley, T. Oswald and R. I. Haines, *Inorg. Chem.*, in press.
10 C. Creutz, *Inorg. Chem.*, *20*, 4449 (1981).
11 R. A. Marcus, *Ann. Rev. Phys. Chem.*, *15*, 155 (1964).
12 C. Creutz, M. Chou, T. L. Netzel, M. Okumara and N. Sutin, *J. Am. Chem. Soc.*, *102*, 1309 (1980).
13 C. T. Lin, W. Böttcher, M. Chou, C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, *98*, 6536 (1976).
14 J. C. Brodovitch, R. I. Haines and A. McAuley, *Can. J. Chem.*, *59*, 1610 (1981).
15 R. J. Crutchley and A. B. P. Lever, *Inorg. Chem.*, *21*, 2276 (1982).
16 B. S. Brunschwig and N. Sutin, *Inorg. Chem.*, *18*, 1731 (1979).
17 G. P. Laroff, R. W. Fessenden and R. H. Schuler, *J. Am. Chem. Soc.*, *94*, 9062 (1972).
18 B. H. J. Bielski, A. O. Allen and H. A. Schwarz, *J. Am. Chem. Soc.*, *103*, 3516 (1981).
19 W. Rybak, A. Haim, T. L. Netzel and N. Sutin, *J. Phys. Chem.*, *85*, 2856 (1981).
20 N. Sutin, *Acc. Chem. Res.*, *15*, 275 (1982); N. Sutin, *Prog. Inorg. Chem.*, *30*, 441 (1983).
21 The radius of the ascorbate species has been calculated [2] to be 3.5 Å.
22 S. Steenken and P. Neta, *J. Phys. Chem.*, *83*, 1134 (1979).
23 E. Pelizzetti, E. Mentasti and E. Baiocchi, *J. Phys. Chem.*, *80*, 2979 (1976).
24 I. Ruff and M. Zimonyi, *Electrochim. Acta*, *18*, 515 (1973).
25 R. C. Young, F. R. Keene and T. J. Meyer, *J. Am. Chem. Soc.*, *99*, 2468 (1977).
26 D. H. Macartney and N. Sutin, *Inorg. Chem.*, in press.
27 G. M. Brown and N. Sutin, *J. Am. Chem. Soc.*, *101*, 883 (1979).
28 C. Greenwood and G. Palmer, *J. Biol. Chem.*, *240*, 3660 (1965).
29 M. Chou, C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, *99*, 5616 (1977).