The Oxidation of Ascorbic Acid by Hexacyanoferrate(III) Ion in Acidic Aqueous Media

Application of the Marcus Cross-Relation

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While theoretical aspects of the Marcus theory for electron-transfer reactions have deserved several articles in *this Journal* (*1–4*), there is a lack of experiments on its application suitable for the undergraduate level. One reaction meeting this purpose is the oxidation of L-ascorbic acid (H_2Asc) by the substitution-inert complex $[Fe(CN)_6]^{3-}$ in acidic medium. The rate for this reaction was found to be first-order in the concentrations of both H_2Asc and $[Fe(CN)_6]^{3-}$, and the overall second-order rate constant, k_{obs}, shown (*5*) to have an inverse dependence on $[H^+]$ over the range of pH examined. Moreover, the same kinetics are followed in the range of temperature 15–30 °C, thus allowing experimental activation parameters to be determined. Values of k_{obs}, at a given temperature and pH, can easily be measured spectrophotometrically by following the decrease in absorbance of $[Fe(CN)_6]^{3-}$ at 418 nm as a function of time. Relating these with the proposed mechanism (*5*), the second-order rate constant for the rate-determining step is obtained at a given temperature. This, in turn, allows comparison with the value predicted on the basis of the Marcus cross-relation.
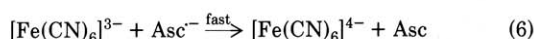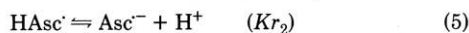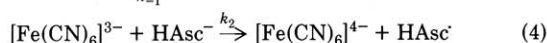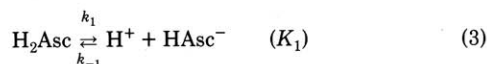
Theory

Many kinetic and mechanistic investigations have been reported on the oxidation of ascorbic acid by a number of outer-sphere metal ion complexes (*5–8*), phenothiazine radicals (*9*), and excited states of metal complexes (*10, 11*). In the present case we consider the oxidation by $[Fe(CN)_6]^{3-}$, with overall stoichiometry

$$2[Fe(CN)_6]^{3-} + H_2Asc \rightleftharpoons 2[Fe(CN)_6]^{4-} + Asc + 2H^+ \qquad (1)$$
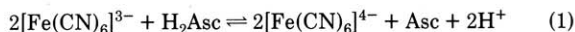
where Asc represents the dehydroascorbic acid formed. The empirical rate law, at constant pH, is

$$-\frac{1}{2}\frac{d[Fe(CN)_6^{3-}]}{dt} = k_{obs}[Fe(CN)_6^{3-}][H_2Asc] \qquad (2)$$

The experimentally measured k_{obs} shows an inverse first-order dependence on $[H^+]$, at constant temperature and ionic strength. In addition, a plot of k_{obs} vs. $[H^+]^{-1}$ is found (*5*) to be linear with zero intercept. This behavior suggests (*5–9, 12*) that ascorbate anion is the kinetically important species. This is oxidized in the slow, rate-determining step (eq 4). A mechanism that is consistent with the kinetic data is (*5–9*),

$$H_2Asc \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H^+ + HAsc^- \qquad (K_1) \qquad (3)$$

$$[Fe(CN)_6]^{3-} + HAsc^- \overset{k_2}{\rightarrow} [Fe(CN)_6]^{4-} + HAsc^{\cdot} \qquad (4)$$

$$HAsc^{\cdot} \rightleftharpoons Asc^{\cdot-} + H^+ \qquad (Kr_2) \qquad (5)$$

$$[Fe(CN)_6]^{3-} + Asc^{\cdot-} \overset{fast}{\rightarrow} [Fe(CN)_6]^{4-} + Asc \qquad (6)$$

Step 6 represents the fast oxidation of the ascorbate radical anion ($pKr_2 = -0.45$, (*13*)) yielding dehydroascorbic acid, a process that may be diffusion-controlled (*7*). An alternative pathway (*7*) that may also account for the disappearance of $Asc^{\cdot-}$ is the disproportionation reaction,

$$Asc^{\cdot-} + Asc^{\cdot-} \overset{H^+}{\rightarrow} H_2Asc + Asc \qquad (7)$$
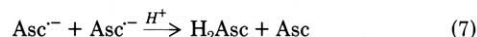
For this reaction an estimated rate constant in excess of 10^8 $M^{-1}s^{-1}$ has been reported (*7*) for $[H^+] = 0.1–1.0$ M. From the above mechanism the rate of disappearance of $[Fe(CN)_6]^{3-}$ can be derived, by applying the steady-state approximation to the concentrations of $HAsc^-$ and $HAsc^{\cdot}$, as

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = \frac{2k_1k_2[H_2Asc][Fe(CN)_6^{3-}]}{k_{-1}[H^+] + k_2[Fe(CN)_6^{3-}]} \qquad (8)$$

Under the experimental conditions of this work, $k_{-1}[H^+] \gg k_2[Fe(CN)_6^{3-}]$ and eq 8 becomes

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = \frac{2k_1k_2[H_2Asc][Fe(CN)_6^{3-}]}{k_{-1}[H^+]} \qquad (9)$$

and by comparison with eq 2 gives

$$k_{obs} = K_1k_2\frac{1}{[H^+]} \qquad (10)$$

This relation allows the second-order rate constant k_2 to be determined, at a given temperature and ionic strength, once k_{obs} values have been measured for different pH values. Our results show that k_{obs} can be reliably measured by using inexpensive and readily available equipment and adopting a somewhat simplified version of a previously used procedure (*5*).

Experimental

Reagents and Apparatus

All chemicals were of the highest purity available and used as received. Doubly distilled water was further purified by a previously described method (*14*). Absorbances were measured with a Bausch and Lomb Spectronic 20 using 1-cm-diameter glass cylindrical cuvettes. A constant-temperature bath was provided by a tank fitted with a Haake Model E 52 constant-temperature circulator, which enabled the temperature to be thermostated to within ±0.5 °C. The pH, which varied in the range 0.50–2.50, was measured with a Radiometer Copenhagen PHM 61 pH meter, fitted with a combined electrode. The pH meter was calibrated with appropriate buffers[2] (*15*) prior to each measurement.

Procedure

Stock solutions: sodium perchlorate (2 M), perchloric acid (0.5 and 1.0 M), $K_3[Fe(CN)_6]$ (8.0×10^{-3} M), and L-ascorbic acid (4.0×10^{-3} M, freshly prepared[3]).

About 50 mL of solution of appropriate ionic strength (1.0 M), and pH (0.50–2.50) is prepared by mixing the above stock solutions, two

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[2] A solution of KH tartrate (saturated at 25 °C), a 0.05 M KH phthalate solution, an equimolar (0.025 M) solution of KH_2PO_4 and Na_2HPO_4, and further checked against a solution of 0.05 M $KH_3(C_2O_4)_2 \cdot 2H_2O$, which have been assigned pH values of 3.56, 4.01, 6.86, and 1.68, respectively, at 25 °C.
[3] Solutions do not need to be deoxygenated if freshly prepared ascorbic acid solution is used.

equal 20-mL portions withdrawn and transferred to separate beakers wrapped with aluminum foil to avoid exposure to light. To one of these solutions is added with mixing 5 mL of $K_3[Fe(CN)_6]$ solution, and to the other 5 mL of ascorbic acid solution. Two 3-mL portions of ascorbic acid buffer mixture are withdrawn and transferred to separate cuvettes. One of these is used as the blank, and the other is wrapped in aluminum foil and placed in the thermostated bath. Similarly, 3 mL of the $K_3[Fe(CN)_6]$ solution is transferred to a cuvette, covered with aluminum foil, placed in the thermostated bath, and left for ~20 min. Equal amounts of the ascorbic acid and $K_3[Fe(CN)_6]$ solutions in the beakers are mixed and the pH determined before and after reaction. Although protons are released in the reaction, there is negligible change in pH under the acid conditions employed. The spectrophotometer is calibrated at 418 nm with the blank, and after thermal equilibration the ascorbic acid and $K_3[Fe(CN)_6]$ solutions in the thermostated cuvettes are mixed, stopwatch started, and the $K_3[Fe(CN)_6]$ absorption is measured at this wavelength ($\epsilon_{418} = 1012$ $M^{-1}cm^{-1}$) as soon as possible after mixing. The cuvette, wrapped in aluminum foil, is then returned to the thermostated bath. Further readings are taken at regular intervals until a degree of reaction of ~80% is reached. As advised above, the cuvette should not be left in the spectrophotometer cavity because after 20 min the temperature of the solution inside rises by ~5 °C, which introduces a considerable error in the determination. Moreover, continuous irradiation by the lamp induces photolysis of $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ (formed both thermal and photochemically) (16) the photoproducts beginning to interfere with the readings after 15–20 min in the cavity.

Results and Discussion

Using this procedure leads to good linear plots of $[Fe(CN)_6^{3-}]^{-1}$ vs. time for degrees of reaction in excess of 80%, thus confirming the overall second-order kinetics. The straight lines for these plots were obtained by least-squares. Values of k_{obs} evolved from this treatment are collected in Table 1. At all temperatures, plots of k_{obs} vs. $[H^+]^{-1}$ were linear over the pH range studied, with intercept zero (see Fig. 1). The resulting slopes $K_1 k_2$, together with the relevant values of K_1 at $\mu = 1.0$ M (17), are collected in Table 2. They were obtained by a least-squares method that minimizes the sum of the squares of the perpendicular distances of the points from the best line (18). This same procedure was used to obtain the activation parameters, for the rate-determin-
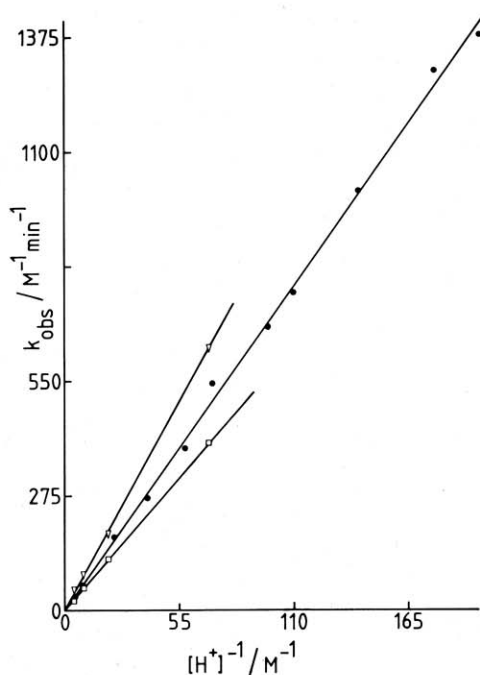
ing step, from the Arrhenius plot of Fig. 2, yielding $\Delta H^{\ddagger} = 4.27 \pm 0.02$ kcal mol^{-1} and $\Delta S^{\ddagger} = -28.29 \pm 1.28$ cal mol^{-1} K^{-1} at 25 °C. These values compare favorably with those obtained for the oxidation of ascorbic acid by other iron(III) metal complexes (6). The recent availability (7, 8) of the rate constant for the self-exchange electron transfer for the couple (HAsc·/HAsc$^-$) together with the experimentally measured (19, 20) self-exchange rate constant for the couple
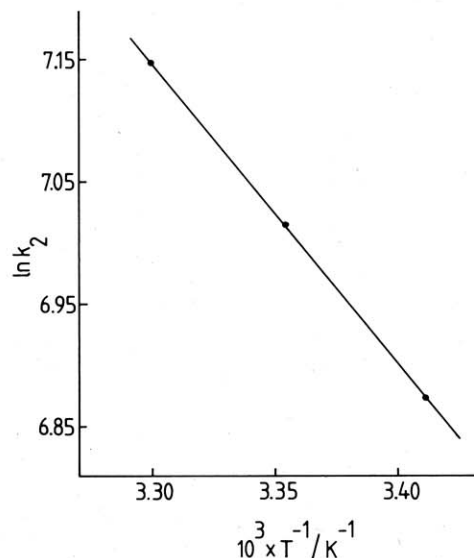

Figure 2. Arrhenius plot for the second-order rate constant k_2.

Table 1. Values of k_{obs} at 293.15, 298.15, and 303.15 K and at Different Acidities[a]

T (K)	k_{obs} (M^{-1}min^{-1})	$[H^+]^{-1}$ (M^{-1})
298.15 ± 0.5	1379.66	199.53
	1294.82	177.80
	1006.65	141.25
	761.59	109.65
	678.15	97.72
	544.00	70.79
	386.56	57.54
	270.65	39.81
	59.85	8.61
	32.53	4.68
293.15 ± 0.5	401.67	69.18
	122.84	20.90
	54.10	8.91
	25.36	4.68
303.15 ± 0.5	630.29	69.18
	180.29	20.90
	85.47	8.91
	45.67	4.68

[a] $\mu = 1.0$ M (Na/HClO$_4$).

Figure 1. Plots of k_{obs} vs. $[H^+]^{-1}$ at $\mu = 1.0$ M and 20 °C (□), 25 °C (●), and 30 °C (▽).

Table 2. Rate Data for the Reaction of $[Fe(CN)_6]^{3-}$ (8.0 × 10^{-4} M) with L-Ascorbic Acid (4.0 × 10^{-4} M) at $\mu = 1.0$ M (Na/HClO$_4$)

T (K)	$K_1 k_2$ (min^{-1})	Intercept (M^{-1}min^{-1})	$10^5 K_1$ (M)[a]	$10^{-2} k_2$ (M^{-1}s^{-1})
293.15	5.80 ± 0.03	0.59 ± 1.91	10.0	9.67
298.15	7.08 ± 0.10	0.42 ± 23.26	10.6	11.13
303.15	9.08 ± 0.11	0.02 ± 6.56	11.9	12.72

[a] Data from ref 17.

([Fe(CN)$_6$]$^{3-}$/[Fe(CN)$_6$]$^{4-}$) makes a Marcus calculation possible. The most useful development of Marcus theory for adiabatic outer-sphere electron-transfer reactions is that which enables the calculation of a cross-reaction rate constant (k_2) from the equilibrium constant (K_{12}) and the rate constants of the corresponding pair of self-exchange reactions (k_{11} and k_{22}) (21, 22),

$$k_2 = (k_{11}k_{22}K_{12}f)^{1/2} \qquad (11)$$

Under certain assumptions (22) the expression for f is

$$\ln f = \frac{(\ln K_{12})^2}{4 \ln (k_{11}k_{22}/Z^2)} \qquad (12)$$

where Z is usually taken as the collision frequency between two uncharged particles in solution (10^{11} M^{-1}s^{-1}). K_{12} is calculated from the reduction potentials of the couples involved under the conditions of measurement; for ([Fe(CN)$_6$]$^{3-}$/[Fe(CN)$_6$]$^{4-}$) the value of 0.448 V vs. NHE was adopted (measured at 25 °C in μ = 0.5064 M with 0.50 M NaClO$_4$ (23)) and for the couple (HAsc$^{\cdot}$/HAsc^{-}) the value of (0.71 ± 0.01) V vs. NHE estimated for μ = 1.0 M from pulse radiolysis data (7, 13) is used. The rate constant k_{11}, for the couple ([Fe(CN)$_6$]$^{3-}$/[Fe(CN)$_6$]$^{4-}$), has been experimentally measured both at low (19) and high (20) cation concentration. It was found (19, 20) that the value of k_{11} depends mainly on the nature and concentration of the cation and not on the anion or ionic strength. While several mechanisms were proposed to account for the catalytic effect of the cations, ion association is thought to play a major role. For a high concentration of Na$^+$ ions (1.75 M) a value of k_{11} = (5.8 ± 0.9) × 10^4 M^{-1}s^{-1} was measured at 32 °C by ^{14}N NMR spectrometry[4] (20). Recent studies (7, 8) involving the oxidation of ascorbic acid, by a number of outer-sphere metal oxidants, led to estimates of 1 × 10^5 and 3 × 10^5 M^{-1}s^{-1} for the self-exchange rate constant, k_{22}, of the couple (HAsc$^{\cdot}$/HAsc^{-}), under the experimental conditions of this work. Use of the latter value together with the parameters above and the Marcus cross-relation (eq 11) yields a calculated value of k_2 = 5.0 × 10^2 M^{-1}s^{-1} at 25 °C in good agreement with the experimental value. A satisfactory agreement is also obtained with k_{22} = 1 × 10^5 M^{-1}s^{-1}, giving k_2 = 3.0 × 10^2 M^{-1}s^{-1} at 25 °C. In either case a successful application of the Marcus cross-relation is illustrated with this calculation. A further check on the validity of the Marcus calculation performed above is made by using the Marcus expression (21, 22) for the rate constant k_2,

$$k_2 = Z \exp (-\Delta G_2^*/RT) \qquad (13)$$

where ΔG_2^* is the free energy of activation for the electron-transfer step, usually approximated by (2)

$$\Delta G_2^* = \Delta G_i^* + \Delta G_o^* + \Delta G_c^* \qquad (14)$$

ΔG_2^* represents the free-energy change required for the activated complex to be formed from the reactant encounter complex. In the Marcus formalism the activated complex is a hypothetical state born out from the necessity of the charge-transfer process to conform to the Franck–Condon energy restrictions, and is best discussed by referring to the potential energy diagram of the reaction (2). Accordingly, prior to the electron-transfer event the donor and acceptor orbitals must have equal energy. This energy equalization is achieved by expending free energy (ΔG_i^*) to carry out the necessary changes in the ligand geometry (inner-sphere reorganization). This, in turn, promotes a rearrangement of the outer solvation sphere of the reactant ions in the activated complex, for which a free-energy change ΔG_o^* is required (outer-sphere reorganization energy). An additional free energy is expended in bringing the charged reactants to the encounter distance in the activated complex (ΔG_c^*). Now, the free energy of activation from Marcus theory (eq 13) is related to the experimentally derived free energy of activated $\Delta G_2^\ddagger$, by (22, 24)

$$\Delta G_2^\ddagger = \Delta G_2^* + RT \ln (kT/Zh) \qquad (15)$$

where k and h are the Boltzmann and Planck constants, respectively. Therefore, the calculated value of $\Delta G^\ddagger$ at 25 °C from eqs 13 and 15 with k_2 = 5 × 10^2 M^{-1}s^{-1}, as calculated above, is $\Delta G^\ddagger$ = 13.77 kcal mol^{-1}. This is in good agreement with the experimental value, derived from the activation parameters, at the same temperature $\Delta G^\ddagger$ = 12.70 kcal mol^{-1}. Finally we note that the value of k_2 = 1.22 × 10^3 M^{-1}s^{-1} measured previously at 15 °C (5) in the presence of K$^+$ ions (μ = 1.0 M), is higher than our value even at 25 °C (see Table 2). This is expected on the basis of Marcus theory since the reduction potential of the couple ([Fe(CN)$_6$]$^{3-}$/[Fe(CN)$_6$]$^{4-}$) is higher in the presence of K$^+$ ions (23) and k_{11} = 5.5 × 10^4 M^{-1}s^{-1} at 15 °C, which is close to that found for the same concentration of Na$^+$ ions at 32 °C (20).

In conclusion, we present a simple, yet reliable, experimental procedure that allows the measurement of the rate constant for the rate-determining step in the oxidation of ascorbic acid by [Fe(CN)$_6$]$^{3-}$. This provides a good opportunity for the student to confirm experimentally the previously proposed mechanism for the overall reaction and enables the student to perform a Marcus calculation on the same system. We feel this is important since the undergraduate student is now exposed to these aspects of the Marcus theory for electron-transfer reactions (25, 26).

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[4] Activation parameters for this self-exchange reaction are only available for K$^+$ ions (1.75 M) between 25 and 40 °C. If the same activation energy is used for Na$^+$ (1.75 M), an estimate of k_{11} = 4.9 × 10^4 M^{-1}s^{-1} at 25 °C is obtained, the difference being within the experimental uncertainty of the determination. Consequently we have used the value measured at 32 °C.