# Mechanistic Study of the Reaction of L-Ascorbic Acid with Hexacyanometalate(III) Ions of Iron(III), Ruthenium(III), and Osmium(III) in Aqueous Acidic Solution at Elevated Pressures

**Nobuyoshi Kagayama, Mitsuhiro Sekiguchi, Yasuhiro Inada, Hideo D. Takagi, and Shigenobu Funahashi***

Laboratory of Analytical Chemistry, Faculty of Science, Nagoya University,
Chikusa, Nagoya 464-01, Japan

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Oxidation reactions of L-ascorbic acid by three hexacyanometalate(III) ions in aqueous acidic media are studied at elevated pressures. Kinetic parameters characterizing two parallel paths involving ascorbic acid ($H_2Asc$) and ascorbate ion ($HAsc^-$), respectively, at 25 °C are as follows: $k_1 = 0.366 \pm 0.016$ $M^{-1}$ $s^{-1}$, $k_2 = (3.6 \pm 0.2) \times 10^2$ $M^{-1}$ $s^{-1}$, $\Delta H_1^{\ddagger} = 34 \pm 2$ kJ $mol^{-1}$, $\Delta H_2^{\ddagger} = 17 \pm 1$ kJ $mol^{-1}$, $\Delta S_1^{\ddagger} = -136 \pm 15$ J $mol^{-1}$ $K^{-1}$, $\Delta S_2^{\ddagger} = -141 \pm 16$ J $mol^{-1}$ $K^{-1}$, $\Delta V_1^{\ddagger} = -40 \pm 68$ $cm^3$ $mol^{-1}$, and $\Delta V_2^{\ddagger} = -14 \pm 3$ $cm^3$ $mol^{-1}$ for hexacyanoferrate reduction; $k_1 = (6.1 \pm 0.3) \times 10^3$ $M^{-1}$ $s^{-1}$, $k_2 = (4.26 \pm 0.22) \times 10^6$ $M^{-1}$ $s^{-1}$, $\Delta H_1^{\ddagger} = 7 \pm 2$ kJ $mol^{-1}$, $\Delta H_2^{\ddagger} = 0 \pm 2$ kJ $mol^{-1}$, $\Delta S_1^{\ddagger} = -149 \pm 17$ J $mol^{-1}$ $K^{-1}$, $\Delta S_2^{\ddagger} = -118 \pm 13$ J $mol^{-1}$ $K^{-1}$, $\Delta V_1^{\ddagger} = -26 \pm 18$ $cm^3$ $mol^{-1}$, and $\Delta V_2^{\ddagger} = -9 \pm 3$ $cm^3$ $mol^{-1}$ for hexacyanoruthenate reduction; $k_1 = 26.7 \pm 1.3$ $M^{-1}$ $s^{-1}$, $k_2 = (4.14 \pm 0.21) \times 10^4$ $M^{-1}$ $s^{-1}$, $\Delta H_1^{\ddagger} = 30 \pm 2$ kJ $mol^{-1}$, $\Delta H_2^{\ddagger} = 9.7 \pm 0.6$ kJ $mol^{-1}$, $\Delta S_1^{\ddagger} = -117 \pm 13$ J $mol^{-1}$ $K^{-1}$, $\Delta S_2^{\ddagger} = -124 \pm 15$ J $mol^{-1}$ $K^{-1}$, $\Delta V_1^{\ddagger} = -90 \pm 75$ $cm^3$ $mol^{-1}$, and $\Delta V_2^{\ddagger} = -10 \pm 3$ $cm^3$ $mol^{-1}$ for hexacyanoosmate(III) reduction. The reaction mechanism was discussed on the basis of the volume profiles of the redox reactions between ascorbic acid and hexacyanometalate ions.

## Introduction

The redox reactions of L-ascorbic acid ($H_2Asc$) and ascorbate ion ($HAsc^-$) in solution had been studied without paying much attention to the structural aspects of this familiar analytical reagent[1-3] until uncertainty concerning the reaction pathways was pointed out by Creutz.[4] The problem of the ascorbic acid oxidation reactions stems from the vague understanding of the structure of the ascorbate radical, i.e., the one-electron oxidation product of ascorbic acid. Since the radical may have a bicyclic structure as its thermodynamically stable form, the estimated redox potential ($E°$) based on the combination of thermodynamic and kinetic parameters[4] may not correspond to the primary outer-sphere oxidation process of ascorbic acid in which the open-chain ascorbate radical is supposed to be formed. Some recent studies still attempt to estimate the electron-exchange rate constants of $H_2Asc^{\bullet +}/H_2Asc$ and $HAsc^{\bullet}/HAsc^-$ redox couples on the basis of the classical Marcus cross relation,[5-9] ignoring this problem, while other studies have been performed to specify the primary oxidation products of ascorbic acid where a rapid ring closure of the ascorbate radical may be included.[10-12] The former approach, however, yielded a consistent second-order rate constant of $1 \times 10^5$ $M^{-1}$ $s^{-1}$ (M = mol $dm^{-3}$) for the $HAsc^{\bullet}/HAsc^-$ couple. A recent study of the oxidation reaction of methyl-substituted ascorbic acid by aquairon(III) ion through the inner-sphere process has revealed that the oxidation of the ascorbate-coordinated iron(III) species by another iron(III) is very slow and that the primary oxidation product of ascorbate ion is bicyclic dehydroascorbic acid, which decomposes to diketogulonic acid under acidic conditions.[13]

In summary of the results reported to date,[11,14,15] the primary oxidation product of ascorbic acid is open-chain dehydroascorbic acid in aprotic solvents, while bicyclic hydrolyzed dehydroascorbic acid is formed in aqueous media. A study by Kwon and Foote[10] suggests that cyclization in the hydroperoxide form of ascorbic acid is relatively slow with a half-life of ca. 5 h at −78 °C, but there is no reason to speculate that the corresponding ring closure in the ascorbate radical is also slow. The plausible species proposed to date are shown in Scheme 1.

H.D.T. has been examining the Marcus theory by utilizing the volume profiles of the outer-sphere electron-exchange reactions[16-18] and has proven that theoretical calculations of activation volumes ignoring any inner-sphere contribution predict the experimental values very well. In this study, the activation volumes of the outer-sphere oxidation reactions of ascorbic acid by hexacyanoferrate(III), hexacyanoruthenate(III), and hexacyanoosmate(III) ions were measured in aqueous acidic media and the reaction mechanism was discussed on the basis of volume profiles.

## Experimental Section

**Materials.** Potassium hexacyanoruthenate(III) was prepared by the oxidation of the corresponding ruthenate(II) ion by Ce(IV) followed by the separation using an ion-exchange method.[8] Potassium hexacyanoosmate(II) trihydrate was provided by mixing aqueous potassium osmate(IV) and potassium cyanide following the literature method.[19]

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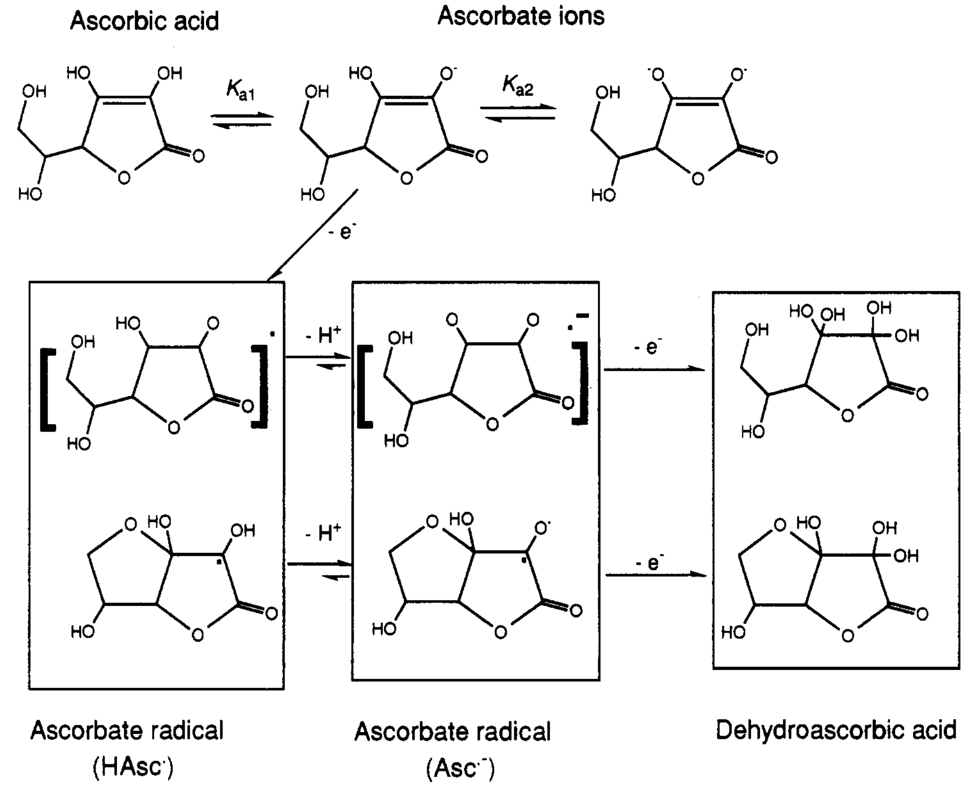
**Scheme 1**



Potassium hexacyanoosmate(III) was obtained by oxidation of the corresponding osmium(III) salt with permanganate followed by separation with the Dowex-50 X8 cation-exchange resin. Other reagents were obtained from Wako Pure Chemicals Inc. and used without further purification. Kinetic and equilibrium measurements were carried out in deaerated doubly distilled water.

**Measurements.** Acid dissociation constants of $H_2Asc$ were measured by a Metrohm 654 pH meter equipped with an AG CH-9101 electrode. Hydrogen ion concentrations of sample solutions were determined after correction by using emf differences from the standard solution at each temperature. The reaction volume for the dissociation of ascorbic acid was measured by dilatometry.[20] Stoichiometry of the reactions was determined by spectrophotometric titration using a Shimadzu UV-265FW spectrophotometer. Kinetic measurements were carried out by a Unisoku RA401 stopped-flow equipment at ambient pressure and by homemade high-pressure stopped-flow equipment (Type Fit-4)[21] at elevated pressures. Kinetic and equilibrium measurements were performed under acidic conditions at a constant ionic strength of 0.10 M with sodium perchlorate. Under pseudo-first-order conditions of a large excess of ascorbic acid over hexacyanometalate(III), reactions were followed mainly at 420.2, 460.0, and 404.4 nm in the ferrate, ruthenate, and osmate systems, respectively.

## Results

Acid dissociation constants of $H_2Asc$ were determined by pH titration at three different temperatures at $I = 0.1$ M ($NaClO_4$).

$$H_2Asc \overset{K_{a1}}{\rightleftharpoons} HAsc^- + H^+ \tag{1}$$

$$HAsc^- \overset{K_{a2}}{\rightleftharpoons} Asc^{2-} + H^+ \tag{2}$$

The results listed in Table 1 are consistent with the literature values.[22] The calculated enthalpy ($\Delta H°$) and entropy ($\Delta S°$) are 8.0 ± 0.4 kJ mol$^{-1}$ and -51 ± 1 J mol$^{-1}$ K$^{-1}$ for $K_{a1}$ and 40 ± 20 kJ mol$^{-1}$ and -90 ± 60 J mol$^{-1}$ K$^{-1}$ for $K_{a2}$, respectively.

**Table 1.** Acid Dissociation Constants of Ascorbic Acid at Various Temperatures and Thermodynamic Parameters at $I = 0.10$ M ($NaClO_4$)[a]

| $T$/°C | p$K_{a1}$ | p$K_{a2}$ |
|---|---|---|
| 15.0 ± 0.1 | 4.118 ± 0.008 | 11.54 ± 0.02 |
| 25.0 ± 0.1 | 4.092 ± 0.005 | 11.50 ± 0.08 |
| 35.0 ± 0.1 | 4.043 ± 0.002 | 11.09 ± 0.02 |
| $\Delta H°$/kJ mol$^{-1}$ | 8.0 ± 0.4 | 40 ± 20 |
| $\Delta S°$/J mol$^{-1}$ K$^{-1}$ | -51 ± 1 | -90 ± 60 |
| $\Delta V_a°$/cm$^3$ mol$^{-1}$ | -9.6 ± 0.2 | |

[a] Quoted errors represent 1 standard deviation.

The reaction volume, $\Delta V_{a1}°$, corresponding to reaction 1 was measured dilatometrically at 25.007 ± 0.002 °C and $I = 0.100$ M ($NaClO_4$). Subtraction of the volume change (21.3 ± 0.1 cm$^3$ mol$^{-1}$) for the neutralization reaction of perchloric acid and sodium hydroxide from the corresponding volume change of the reaction between ascorbic acid and sodium hydroxide yielded -9.6 ± 0.2 cm$^3$ mol$^{-1}$. This value falls within the ordinary range of reaction volumes of dissociation reactions of weak organic acids.[23]

Stoichiometry measurements of the oxidation reactions of ascorbic acid by hexacyanometalate(III) ions, $M(CN)_6^{3-}$, proved that ascorbic acid is a two-electron reductant, as has been reported in previous studies.[4,24] Under pseudo-first-order conditions at constant hydrogen ion concentration, the rate followed excellent first-order kinetics with respect to the hexacyanometalate concentration. Thus, the rate law is given by the following equations:[5,24]

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$$-d[M(CN)_6^{3-}]/dt = k_0[M(CN)_6^{3-}]$$

$$k_0 = 2C_{Asc}(k_1 + K_{a1}k_2[H^+]^{-1})/(1 + K_{a1}[H^+]^{-1}) \quad (3)$$

where $k_0$ is the conditional first-order rate constant including both the total concentration of ascorbic acid ($C_{Asc}$) and concentration of hydrogen ion. For each metalate system, it has been confirmed that $k_0$ values at a constant pH (pH = $-\log([H^+]/mol\ dm^{-3})$) are proportional to $C_{Asc}$ (supplementary material: Tables SI–SIII). Thus the rate is first order in the total concentration of ascorbic acid. $k_0$ values over the pH range 1.0–2.0 were obtained at several temperatures and at ambient pressure (Table SIV–SVI). In Figure 1 are shown the typical plots of $k_0/C_{Asc}$ vs $[H^+]^{-1}$ at each temperature, which lie on a straight line with an intercept. Under the present experimental conditions, $K_{a1}[H^+]^{-1}$ in the denominator of eq 3 is negligible. Thus the slope and intercept of the plots were attributed to $K_{a1}k_2$ and $k_1$, respectively. The rate constants and activation parameters at ambient pressure are listed in Table 2.

$k_0$ values were also determined at various pressures up to 61 MPa (Tables SVII–SIX). Figure 2 shows the pressure dependence of $k_1$ and $K_{a1}k_2$. The activation volume $\Delta V^*$ was evaluated according to the relation $k = k^0 \exp(-\Delta V^*/RT)$ accepting no pressure dependence of the activation volume. Dilatometrically obtained $\Delta V_{a1}°$ was used for the calculation of $\Delta V_2^*$. $\Delta V_1^*$ and $\Delta V_2^*$ values corresponding to $k_1$ and $k_2$ processes are listed in Table 2.

## Discussion

Under the acid concentration range 0.1–0.001 M, only $H_2Asc$ and $HAsc^-$ are the reactive species, according to the p$K$ values. Since hexacyanometalate(III) ions are substitution inert and anionic, a plausible reaction pathway is through the outer-sphere mechanism. By considering the reported reactivity of ascorbate radical species,[4] the only stable form of the ascorbate radical seems to be naked $Asc^{\bullet-}$ rather than $H_2Asc^{\bullet+}$ and/or $HAsc^\bullet$, and the acid dissociation processes of the latter two species are almost diffusion-controlled.

$$\begin{tikzcd}
H_2Asc + M(CN)_6^{3-} \arrow[r, shift left, "k_1"] \arrow[d, shift right] & H_2Asc^{\bullet+} + M(CN)_6^{4-} \arrow[l, shift left] & (4) \\
HAsc^- + M(CN)_6^{3-} \arrow[u, shift right, "H^+"'] \arrow[r, shift left, "k_2"] & HAsc^\bullet + M(CN)_6^{4-} \arrow[l, shift left] & (5)
\end{tikzcd}$$

$$H_2Asc^{\bullet+} \rightleftharpoons HAsc^\bullet + H^+ \quad (6)$$

$$HAsc^\bullet \rightleftharpoons Asc^{\bullet-} + H^+ \quad (7)$$

As the resulting $Asc^{\bullet-}$ is a strong reducing reagent ($E°$ = –0.12 to –0.16 V),[4] it will either reduce another $M(CN)_6^{3-}$ or disproportionate to produce dehydroascorbic acid and ascorbate anion, depending on the reactivity and concentration of oxidizing reagents.[24]

$$Asc^{\bullet-} + M(CN)_6^{3-} \rightarrow M(CN)_6^{4-} + \text{dehydroascorbic acid} \quad (8)$$

$$2Asc^{\bullet-} + 1 \text{ or } 2H^+ \rightarrow HAsc^- \text{ or } H_2Asc + \text{dehydroascorbic acid} \quad (9)$$

In either case, the stoichiometry of the reaction is 1:2. By considering the rather high redox potentials reported for $H_2Asc$ and $HAsc^-$, 1.17 and 0.723 V, respectively, it seems reasonable to speculate that the rate-determining step is the slow outer-sphere electron-transfer process defined by reactions 4 and 5. At this stage it is not known whether the produced radical species is in a monocyclic form or in a bicyclic form. As suggested by Sisley and Jordan,[13] if the bicyclic intermediate is thermodynamically more stable than the monocyclic parent radical, the estimation of electron-exchange rate constants, $k_{11}$ and $k_{11}'$ for $H_2Asc/H_2Asc^{\bullet+}$ and $HAsc^-/HAsc^\bullet$ couples, respectively, by the Marcus cross relation may provide rather small values, as the corresponding redox potentials used for the calculation include the ring-closure process.

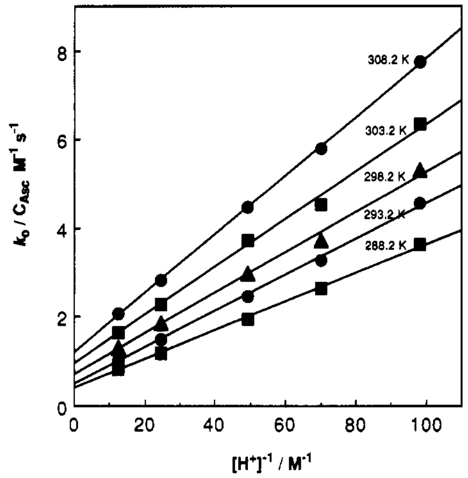

**Figure 1.** Dependence of conditional rate constants for the reduction of hexacyanoferrate(III) ion by ascorbic acid on $[H^+]^{-1}$ at various temperatures.

Electron-transfer reactions of hexacyanometalate ions are known to exhibit strong dependence on the concentration of cations.[14b,25,26] Swaddle et al.[27,28] reported the volume profiles of the electron exchange in $Fe(CN)_6^{3-/4-}$ and concluded that the large positive volume of activation cannot be attributed to the simple charge cancellation by ion pair formation. Recent studies by Hoddenbagh and Macartney[29] suggest that the application of the Marcus cross relation to cross reactions with the use of electron-exchange rate constants of hexacyanometalate complexes obtained at a constant ionic strength is still valid. If this is the case, the Marcus cross relation predicts a simple linear relation between the redox potentials ($-FE°$) of oxidants and the activation free energies ($\Delta G^*$) of each cross reaction with a slope of $^1/_2$, assuming that ascorbic acid and ascorbate ion behave in the same manner for all reactions. Figure 3 shows that the plots of $\Delta G^*$ vs $-FE°$ of three hexacyano complexes are linear for both $H_2Asc$ and $HAsc^-$ oxidation reactions with slopes of 0.45 ± 0.05 and 0.45 ± 0.05, respectively. These results suggest that primary one-electron oxidation products of ascorbic acid ($H_2Asc$) and ascorbate ion ($HAsc^-$), respectively, are the same for all three reactions. Thus it is possible to estimate the redox potentials of ascorbic acid and ascorbate ion for the formation of each unknown but unique one-electron-oxidation product. As the electron-exchange rate constants for the three hexacyanometalate(II/III) couples are all in the order of $10^4$ $M^{-1}$ $s^{-1}$,[30] the redox potential for one-electron oxidation of $HAsc^-$ is estimated to be 0.70 ± 0.05 V, with the assumption that the electron-exchange rate constant of the $HAsc^-/HAsc^\bullet$ couple is $10^5$ $M^{-1}$ $s^{-1}$.[5] A value of 0.95 ± 0.05 V was obtained by using $1 \times 10^5$ $M^{-1}$ $s^{-1}$ for the electron-exchange rate constant of the $H_2Asc/H_2Asc^{\bullet+}$ couple.[8] The consistency of the results obtained here with those reported before,[4,24] however, does not necessarily mean the validity of the electron-exchange rate constants of ascorbic acid and ascorbate ion estimated from

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**Table 2.** Rate Constants and Activation Parameters for Oxidation Reactions of Ascorbic Acid by Hexacyanometalate(III) Ions[a]

| $M(CN)_6^{3-}$ | $k_i$(25.0 °C)/$M^{-1}$ $s^{-1}$ | $\Delta H^‡$/kJ $mol^{-1}$ | $\Delta S^‡$/J $mol^{-1}$ $K^{-1}$ | $\Delta V^‡$/$cm^3$ $mol^{-1}$ |
|---|---|---|---|---|
| $Fe(CN)_6^{3-}$ | $k_1$: 0.366 ± 0.016 | 34 ± 2 | −136 ± 15 | −40 ● 68 |
| | $k_2$: (3.6 ± 0.2) × $10^2$ | 17 ± 1 | −141 ± 16 | −14 ± 3 |
| $Ru(CN)_6^{3-}$ | $k_1$: (6.1 ± 0.3) × $10^3$ | 7 ± 2 | −149 ± 17 | −26 ± 18 |
| | $k_2$: (4.26 ± 0.22) × $10^6$ | 0 ± 2 | −118 ± 13 | −9 ± 3 |
| $Os(CN)_6^{3-}$ | $k_1$: 26.7 ± 1.3 | 30 ± 2 | −117 ± 13 | −90 ± 75 |
| | $k_2$: (4.14 ± 0.21) × $10^4$ | 9.7 ± 0.6 | −124 ± 15 | −10 ± 3 |

[a] Quoted errors represent 1 standard deviation.

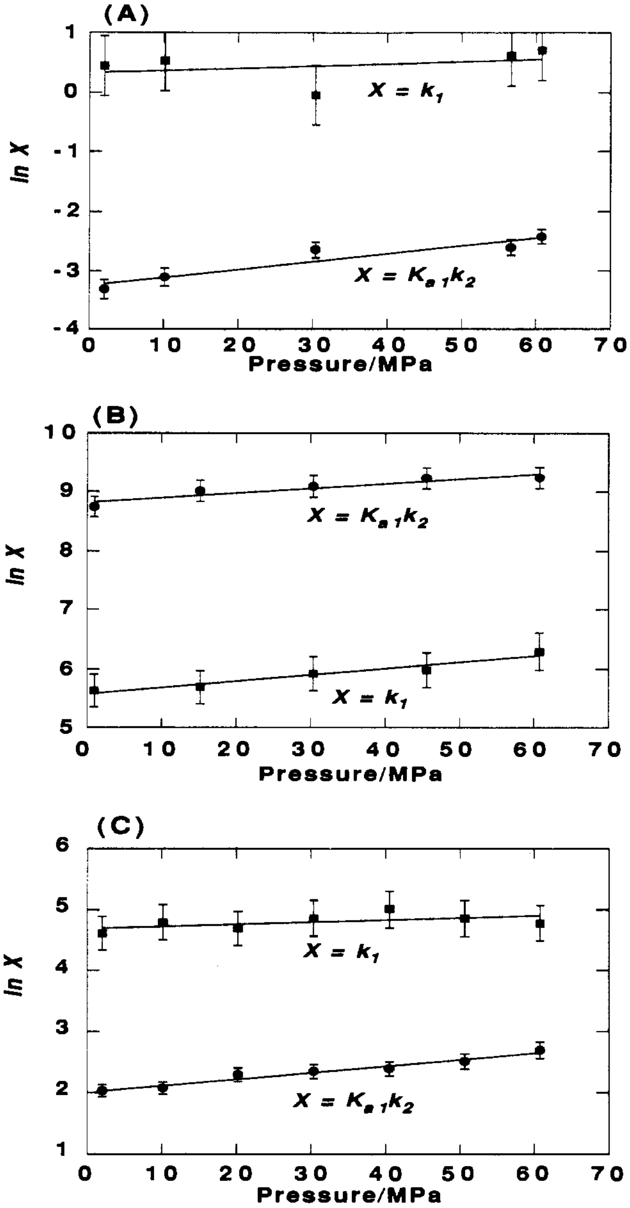

**Figure 2.** Pressure dependence of $k_1$(■) and $K_{a1}k_2$ (●): (A) reaction of hexacyanoferrate(III); (B) reaction of hexacyanoruthenate(III); (C) reaction of hexacyanoosmate(III). Error bars represent standard deviations estimated according to the law of propagation of errors.

the Marcus theory, since the Marcus-type cross relation can be observed in any reaction system where the activation process for each reactant is independent of the other reactant and the activated species are the same for the electron-exchange and cross reactions.[31] Thus the consistency of the results so far obtained merely suggests that $HAsc^-$ or $H_2Asc$ is activated in the same manner to produce each common oxidation product for both electron-exchange and cross reactions. Therefore, there is still no evidence to speculate that the redox potentials used for the estimation of $k_{11}$ and $k_{11}'$ correspond to the exact outer-sphere radical formation processes. Volume analysis, however, may be used to examine the applicability of the cross relation to the ascorbate oxidation reactions.[16-18]

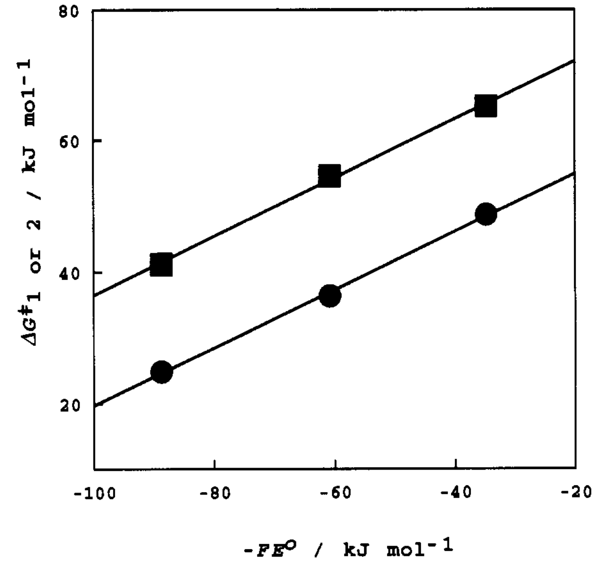

**Figure 3.** Plots of $\Delta G^‡$ vs $-FE°$ for the reactions of hexacyanometalate(III) ions with ascorbic acid ($H_2Asc$, ■) and ascorbate ion ($HAsc^-$, ●).

As the accumulated errors are very large, further discussion on $\Delta V_1^‡$ values may not be fruitful. Thus the discussion is focused on the reaction expressed by eq 5. The following equations are readily derived by differentiation of the respective free energy terms in the Marcus cross relation by pressure:

$$\Delta V_{12}^‡ = [(\Delta V_{11}^‡ + \Delta V_{22}^‡ + \Delta V_{12}°)/2] + C \qquad (10)$$

$$C = [X\Delta V_{12}° \ln K_{12} - 2(\ln K_{12})^2(\Delta V_{11}^‡ + \Delta V_{22}^‡)]/X^2$$

$$X = 4 \ln (k_{11}k_{22}/Z^2)$$

where $\Delta V_{12}^‡$ is the activation volume of the cross reaction, $\Delta V_{11}^‡$ and $\Delta V_{22}^‡$ are the activation volumes of each electron-exchange reaction, and $\Delta V_{12}°$ is the volume change of the cross reaction. $k_{11}$, $k_{22}$, and $Z$ are the rate constants of each electron-exchange reaction and the collision frequency, which is usually taken to be $10^{11}$ $M^{-1}$ $s^{-1}$, respectively. When the reaction is not too exoergic, the value of $C$ is very small and the resulting equation is exactly the same form as that obtained from Ratner and Levine's equation.[31] The activation volume of the $HAsc^•/HAsc^-$ electron-exchange reaction can be calculated from the volume expression of the Marcus theory.[16-18] Without considering the structural changes, the activation volume is calculated to be −5.8 $cm^3$ $mol^{-1}$ with the use of 500 pm for the radii of $HAsc^-$ and $HAsc^•$.[8] As the reported activation volume for the $Fe(CN)_6^{3-/4-}$ electron-exchange reaction, $\Delta V_{22}^‡$, is +22 $cm^3$ $mol^{-1}$,[27] the reaction volume corresponding to eq 5 is −44 ± 4 $cm^3$ $mol^{-1}$. By the use of −36 ± 1 $cm^3$ $mol^{-1}$ as $\Delta V°$ for the redox equilibrium between $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$,[28] the reaction volume corresponding to the

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formation of HAsc• from $HAsc^-$ is calculated to be the negative value of $-8 \pm 4$ $cm^3$ $mol^{-1}$.

Formation of HAsc• from $HAsc^-$ causes less electrostriction, and the volume change should be a moderately positive value.[23] By considering the elongation of the C–C bond accompanying the radical formation, which also causes positive volume change, the reaction volume of $-8 \pm 4$ $cm^3$ $mol^{-1}$ estimated here is too negative for a simple one-electron oxidation reaction of the ascorbate ion. If the ascorbate radical is in bicyclic form, however, the reaction volume corresponding to the ascorbate radical formation reaction from ascorbate ion should have a large negative value as the formation of the five-membered ring usually exhibits a value of $-15$ $cm^3$ $mol^{-1}$.[32] Further negative contribution arises if the acid dissociation of the ascorbate radical is also involved in the reaction. However, the formation of dissociated bicyclic ascorbate radical, $Asc^{\bullet-}$, in the redox equilibrium corresponding to the electron-transfer reaction may not fulfill the original assumption that the electron exchange between $HAsc^-$ and HAsc• occurs through a simple outer-sphere process.

If nonadiabaticity is taken into account in the electron-exchange reaction between the ascorbate ion and ascorbate radical, its contribution to the activation volume will be calculated by eq 11,[16] where $\alpha$, $\beta$, and $\sigma$ are a distance scaling factor, the isothermal

$$\Delta V^{\ddagger}_{NA} = -2RT\alpha\beta\sigma/3 \qquad (11)$$

compressibility of solvent, and the distance of closest approach between two reactants, respectively. With the use of $\alpha = 10$ $nm^{-1}$,[16,23] $\beta = 4.6 \times 10^{-4}$ $MPa^{-1}$, and $\sigma = 1000$ pm, the $\Delta V^{\ddagger}_{NA}$ value for the electron exchange of the $HAsc^{\bullet}/HAsc^-$ couple is estimated to be $-8$ $cm^3$ $mol^{-1}$. As the plots in Figure 3 suggest that all activated species involved in the reactions are the same for the self-exchange and the cross reactions, the volume expression given in eq 10 is still valid even for a nonadiabatic process.[31] A value of about 0 $cm^3$ $mol^{-1}$ is obtained for the reaction volume corresponding to the formation of the ascorbate radical from the ascorbate ion by this calculation. The obtained reaction volume may still be smaller than the expected value for the simple one-electron oxidation process of the ascorbate ion, for which a more positive value should be expected. However, a combination of nonadiabaticity with possible ring-closure and/or acid dissociation from the ascorbate radical may explain the experimentally obtained activation volume of the cross reaction.

Furthermore, similar results were also obtained from analysis of other reactions with $Ru(CN)_6^{3-}$ and $Os(CN)_6^{3-}$ based on the assumption that the activation volumes of each $M(CN)_6^{3-/4-}$ couple are similar to that of the $Fe(CN)_6^{3-/4-}$ couple. Thus, volume analysis of ascorbate oxidation reactions indicates that the reactions do not go through a simple adiabatic process. An involvement of a bicyclic ascorbate radical and/or a nonadiabatic pathway may be suggested as alternative mechanisms. It is concluded that the electron-exchange rate constants for $H_2Asc^{\bullet+}/H_2Asc$ and $HAsc^{\bullet}/HAsc^-$ couples reported to date may not correspond to the hypothetical outer-sphere electron-exchange process considered in the Marcus theory.

## Conclusion

In this study, the volume profiles of the redox reactions between ascorbic acid and hexacyanometalate(III) ions were demonstrated for the first time.[9c] It was indicated that the oxidation reactions of ascorbic acid may not proceed through a simple adiabatic process but through a more complicated way with possible formation of a bicyclic intermediate and that the electron-exchange rate constants of the $HAsc^{\bullet}/HAsc^-$ couple so far estimated[5–9] from the Marcus cross relation may not be valid.

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**Supplementary Material Available:** Listings of conditional rate constants for the ascorbate oxidation reactions at various concentrations of ascorbic acid (Tables SI–SIII), at various temperatures and pH's (Tables SIV–SVI), and at various pressures (Tables SVII–SIX) (8 pages). Ordering information is given on any current masthead page.