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Kinetics and mechanism of the reduction of pentacyanonitroferrate(III) by L-ascorbic acid in acidic aqueous solution

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The electron transfer reaction between $[Fe(CN)_5(NO_2)]^{3-}$ and ascorbic acid was subjected to a detailed kinetic and thermodynamic study as a function of pH, ascorbic acid concentration, temperature and pressure. The pH profile indicates a pH independent region in the pH 5.0–5.5 range, which is ascribed to the oxidation of the ascorbate anion HA^- present in solution under such conditions. The experimental rate and activation parameters suggest that this redox process follows an outer-sphere electron transfer mechanism. The Marcus, Fuoss and Stranks–Marcus–Hush relationships were applied to estimate the self-exchange rate constant for the $[Fe(CN)_5(NO_2)]^{3-/4-}$ couple, the ion-pair formation constant, the rate constant for electron transfer and the value of $\Delta V^{\ddagger}_{et}$. The results are discussed in reference to related systems reported in the literature.

An increasing interest exists in the study of electron transfer processes that are important in biological systems. The oxidation of L-ascorbic acid (vitamin C) by transition metal complexes in aqueous solution is one of these. It is known that ascorbate exists in cellular systems at relatively high concentration[1] and is an important cellular antioxidant.[2] Reactions of ascorbic acid with various inorganic oxidants have recently been investigated in much detail.[3–18] We have extended our studies to include the reaction between ascorbic acid and pentacyanonitroferrate(III). Our interest in the reduction of $[Fe(CN)_5(NO_2)]^{3-}$ by ascorbic acid results from specific properties of the nitro complex and its potential application as a hypotensive agent. Pentacyanonitroferrate(III) together with sodium nitroprusside, molsidomine and nitroglycerin belongs to the group of drugs referred to as nitrovasodilators.[18] The relaxation of smooth muscle caused by the action of these compounds is connected with their ability to produce nitric oxide, NO. From the biochemical point of view the interaction of nitrovasodilators with cellular antioxidants is particularly important as it can be one of the decisive steps in their metabolism.

It was previously found[3,4] that pseudo-first-order rate constants for the oxidation reactions of L-ascorbic acid by metal complexes exhibit a characteristic pH dependence due to both the acid dissociations of ascorbic acid (H_2A) and the hydrolysis equilibria of the oxidant when it involves an aquated metal ion. Many of these reactions proceed according to an outer-sphere electron transfer process since the oxidant is an inert metal complex and does not posses vacant co-ordination sites, *viz.* $Fe(CN)_6{}^{3-}$, $Fe(phen)_3{}^{3+}$, $Co(bipy)_3{}^{3+}$, $Co(phen)_3{}^{3+}$, $Co(C_2O_4)_3{}^{3-}$, *etc.*[3,13–16] However, in other systems where the metal complex has labile co-ordination sites, for example in aquated Mn^{III}, Co^{III} and Fe^{III}, kinetic evidence for the operation of an inner-sphere electron transfer process was presented.[11,17]

In recent years high-pressure techniques have been applied to the study of bioinorganic reaction systems. Their application in the study of inter- and intra-molecular electron transfer reactions of co-ordination complexes in solution has added a new dimension to improve the understanding of the intimate reaction mechanism.[19–21] Here we report our investigations on the outer-sphere electron transfer reaction between a low and high charged anionic species, *viz.* the ascorbate anion HA^- and the $[Fe(CN)_5(NO_2)]^{3-}$ complex ion, respectively. For this system a pH, temperature and pressure dependence study was performed and the activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta V^{\ddagger}$) are reported. Theoretical calculations based on the Marcus, Fuoss and Stranks–Marcus–Hush relationships were employed to estimate the self-exchange rate constant for the $[Fe(CN)_5(NO_2)]^{3-/4-}$ couple, the ion-pair formation constant, the rate constant for electron transfer, and to account for the experimentally observed pressure effects.

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Experimental

Materials

Potassium pentacyanonitroferrate(III), $K_3[Fe(CN)_5(NO_2)]$, was prepared as described before[22] and its purity checked by elemental analyses, IR and UV/VIS spectroscopy. All other chemicals were of analytical reagent grade and used without further purification. Solutions were prepared with deionized (Millipore) water and purged with N_2 for *ca.* 15 min prior to use. An acetate buffer solution and NaOH were used to control the pH in the range 4.0–5.6, whereas a phosphate buffer and NaOH were employed for pH > 5.6. The ionic strength of the test solutions (0.3 M) was adjusted by the addition of NaCl.

Measurements

pH Measurements were performed on a Metrohm 623 pH meter equipped with a Sigma glass electrode. The UV/VIS spectra were recorded on a Shimadzu UV-2100 spectrophotometer equipped with a thermostatted cell compartment CPS-260. Kinetic measurements were performed on a thermostatted (±0.1 °C) stopped-flow SX-17MV spectrophotometer from Applied Photophysics and on a home-made high-pressure stopped-flow unit[23,24] at pressures up to 120 MPa. The kinetic traces were recorded on a IBM compatible computer and analysed with the OLIS KINFIT (Bogart, GA, 1989) set of programs. The redox process was followed at 384 nm, the absorbance maximum for $[Fe(CN)_5(NO_2)]^{3-}$. All kinetic experiments were performed under pseudo-first-order conditions, *i.e.* at least a ten-fold excess of ascorbic acid. The studied reactions exhibit excellent pseudo-first-order behaviour for at least three half-lives. The reported rate constants are

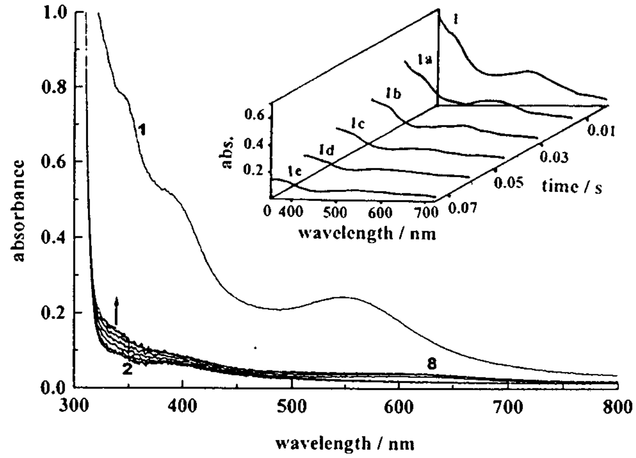

Fig. 1 Repetitive scan spectra for the reduction of $[Fe(CN)_5(NO_2)]^{3-}$ by ascorbate anion. Experimental conditions: $[Fe^{III}] = 1 \times 10^{-3}$ M, $[H_2A]_t = 0.015$ M, 25 °C, pH 5.3, $I = 0.3$ M. Curves: 1, spectrum before mixing the reaction components; 1a–1e, spectra related to the first step of the redox reaction, $\Delta t = 1.25 \times 10^{-2}$ s, the total time, $t = 7.5 \times 10^{-2}$ s; 2–8, spectra related to the further reduction of $[Fe(CN)_5(NO)]^{2-}$ to iron(I) species, $\Delta t = 10$ min, the total time, $t = 60$ min

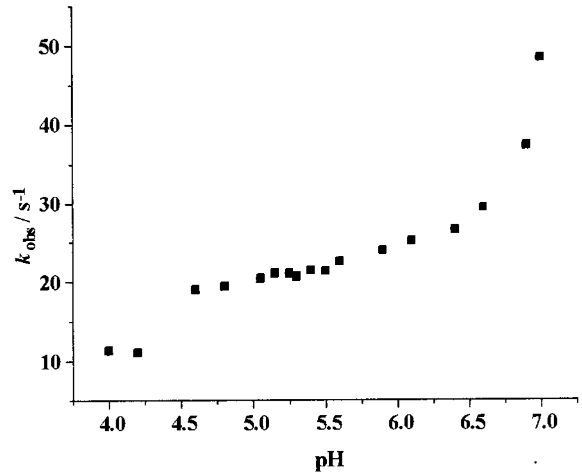

Fig. 2 pH Dependence of k_{obs} for the reduction of $[Fe(CN)_5(NO_2)]^{3-}$ by ascorbic acid. Experimental conditions: $[Fe^{III}] = 5 \times 10^{-4}$ M, $[H_2A]_t = 0.015$ M, 25 °C, $I = 0.3$ M

$$[Fe(CN)_5(NO_2)]^{3-} \xrightarrow[\text{first step, fast}]{H_2A} [Fe(CN)_5(NO_2)]^{4-} \underset{OH^-}{\overset{H_2O}{\rightleftharpoons}} [Fe(CN)_5(NO)]^{2-}$$

$$[Fe(CN)_5(NO)]^{2-} \xrightarrow[\text{second step, slow}]{H_2A} [Fe(CN)_5(NO)]^{3-} \underset{\text{fast}}{\overset{-CN^-}{\rightleftharpoons}} [Fe(CN)_4(NO)]^{2-}$$

Scheme 1

$$H_2A + 2[Fe(CN)_5(NO_2)]^{3-} \xrightarrow{\text{slow}} A + 2H^+ + 2[Fe(CN)_5(NO_2)]^{4-}$$

$$2[Fe(CN)_5(NO_2)]^{4-} \underset{OH^-}{\overset{H_2O,\ \text{fast}}{\rightleftharpoons}} 2[Fe(CN)_5(NO)]^{2-}$$

Scheme 2

the mean from at least five kinetic runs, and the quoted uncertainties are based on one standard deviation.

Results and Discussion

The reduction of pentacyanonitroferrate(III), $[Fe(CN)_5(NO_2)]^{3-}$ by ascorbic acid proceeds in two steps. The first step involves reduction of the iron(III) complex to Fe^{II} and occurs on a stopped-flow timescale. The characteristic spectral changes shown in Fig. 1 (see curves 1a–1e and 2) indicate that this reaction leads to formation of the pentacyanonitrosylferrate(II) ion, $[Fe(CN)_5(NO)]^{2-}$. In fact the $[Fe(CN)_5(NO_2)]^{3-}$ complex is reduced to the $[Fe(CN)_5(NO)_2]^{4-}$ species, but under our selected conditions the formation of the latter is not detectable due to its high instability in aqueous solutions at pH < 11. In acidic media pentacyanonitroferrate(II) is rapidly converted into the $[Fe(CN)_5(NO)]^{2-}$ complex.[25,26] The pentacyanonitrosylferrate(II) complex undergoes slowly further reduction by ascorbic acid to iron(I) species, *viz.* $[Fe(CN)_5(NO)]^{3-}$ and $[Fe(CN)_4(NO)]^{2-}$ (see Fig. 1, curves 2–8).[27] For the above described redox processes we propose the overall reaction sequence in Scheme 1.

The kinetics of the first step (Scheme 1) of the reduction of $[Fe(CN)_5(NO_2)]^{3-}$ by ascorbic acid was investigated in detail. The redox process involves the oxidation of ascorbic acid to dehydroascorbic acid as indicated in Scheme 2. The oxidation reaction of ascorbic acid strongly depends on pH, as found previously for other oxidants.[3,4,10–12] This phenomenon can be correlated with the different reactivities of the actual ascorbic acid/ascorbate species present in solution. Under the selected experimental conditions, *i.e.* a large excess of ascorbic acid, the reactions followed pseudo-first-order kinetics. The plot of k_{obs} *versus* pH reported in Fig. 2 demonstrates that the pH dependence reaches a plateau in the pH range 5.0–5.5, which is followed by a significant increase in the observed rate constants at higher pH.

These data are in good agreement with results expected on the basis of the acid dissociation constants for ascorbic acid.[7,8] According to these under the selected conditions ($T = 25$ °C and $I = 0.3$ M) mainly HA^- species will exist in the range of the plateau (at pH ≈ 5) and participate in the rate-determining step. At higher pH, A^{2-} ions formed in solution under such conditions cause a drastic increase in k_{obs} because of their significantly stronger oxidation ability. It should be noted that a similar pH dependence was reported by Bänsch *et al.*[3] for a related system, namely $[Fe(CN)_6]^{3-}$–ascorbic acid. They also found that in the lower pH range (< 1.0) there is another plateau which can be ascribed to the redox reaction mainly associated with H_2A.

All temperature and pressure studies reported in this work were performed in the pH independent region (5.3). In this region small variations in pH as a result of changes in temperature and pressure will not significantly affect the values of k_{obs}. It was previously found[26] that pentacyanonitroferrate(III) is relatively stable at this pH. In more acidic media, acid-catalysed aquation occurs with $[Fe(CN)_5(H_2O)]^{2-}$ as the reaction product, whereas in basic media (pH > 10) hydrolysis to $[Fe(CN)_5(OH)]^{3-}$ takes place. Owing to the selected reaction conditions, participation of these species in the oxidation reaction of ascorbic anion was not taken into account.

In the studied system the reactions (1)–(3) have to be considered since HA^- is the main species present in solution under the selected conditions. Under pseudo-first-order conditions the rate law for these reactions is given in equation (4) where

$$H_2A \overset{K_1}{\rightleftharpoons} HA^- + H^+ \quad (1)$$

$$HA^- + [Fe(CN)_5(NO_2)]^{3-} \xrightarrow{k} [Fe(CN)_5(NO_2)]^{4-} + HA^{\bullet} \quad (2)$$

$$HA^{\bullet} + [Fe(CN)_5(NO_2)]^{3-} \xrightarrow{\text{fast}} [Fe(CN)_5(NO_2)]^{4-} + A + H^+ \quad (3)$$

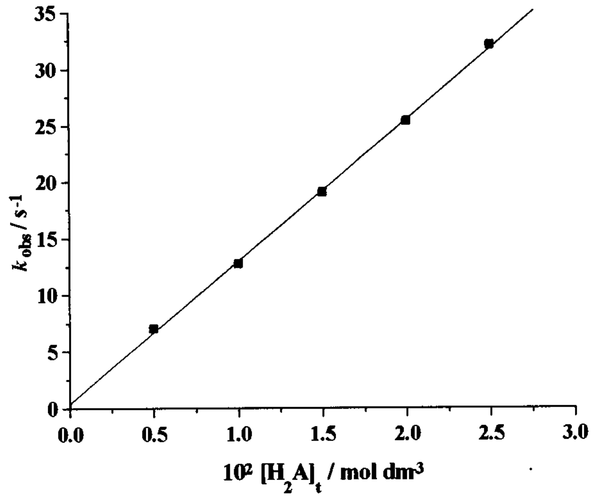

Fig. 3 Concentration dependence of k_{obs} for the reduction of [Fe(CN)$_5$(NO$_2$)]$^{3-}$ by ascorbate anion. Experimental conditions: [Fe^{III}] = 5×10^{-4} M, 25 °C, I = 0.3 M, pH 5.3

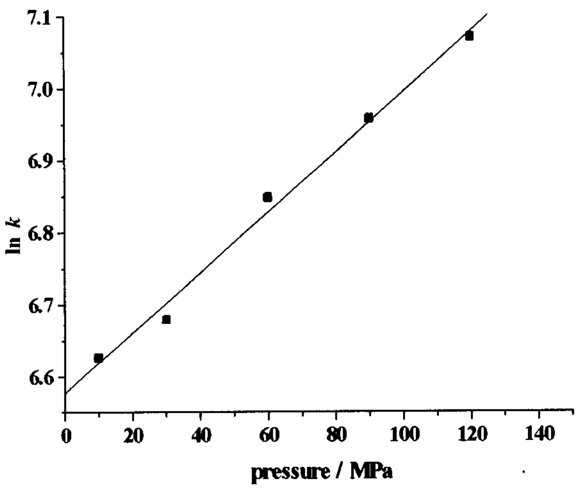

Fig. 4 Plot of ln k *versus* pressure for the reduction of [Fe(CN)$_5$(NO$_2$)]$^{3-}$ by ascorbate anion. Experimental conditions: [Fe^{III}] = 5×10^{-4} M, [H$_2$A]$_t$ = 0.015 M, 15 °C, I = 0.3 M, pH 5.3

$$-\frac{d[Fe^{III}]}{dt} = \frac{2kK_1}{[H^+] + K_1}[H_2A]_t[Fe^{III}] \qquad (4)$$

[H$_2$A]$_t$ represents the total ascorbate concentration. Under these conditions, *i.e.* [H$_2$A]$_t \gg$ [Fe^{III}], the expression for k_{obs} is as in equation (5). On the basis of this equation, k_{obs} should

$$k_{obs} = \frac{2kK_1}{[H^+] + K_1}[H_2A]_t \qquad (5)$$

increase linearly with increasing total ascorbate concentration. As shown in Table 1 and Fig. 3 the dependence of k_{obs} on [H$_2$A]$_t$ is linear, from which it follows that $k = 645 \pm 8$ M^{-1} s^{-1} (at 25 °C and I = 0.3 M; pK_1 = 3.6).

The presence of a small intercept in the plot in Fig. 3 can be assigned to experimental error and indicates that there is no significant contribution from reverse or other parallel reaction paths. The large value of the rate constant k is characterised by a relatively low activation enthalpy, $\Delta H^\ddagger = 21 \pm 2$ kJ mol^{-1} (see Table 2). The activation entropy found for this process is very negative, $\Delta S^\ddagger = -119 \pm 6$ J K^{-1} mol^{-1}, and could result from the formation of a highly ordered transition state.

As can be seen from the results reported in Table 1, the observed rate constant increases with increasing pressure. The pressure dependence of the second-order rate constant (Fig. 4) resulted in a negative activation volume, $\Delta V^\ddagger = -10.0 \pm 0.5$ cm^3 mol^{-1}. A meaningful decrease in partial molar volume during the redox process can be ascribed to the increase in electrostriction due to significant charge concentration on going from 3- to 4-charged complex species during the electron transfer process.

It is informative to compare the results of the present system with those reported earlier for the related system [Fe(CN)$_6$]$^{3-}$–ascorbate anion.[3] The values of the second-order rate constants and activation parameters summarized in Table 2 indicate that k, $\Delta G^\ddagger$, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for [Fe(CN)$_5$(NO$_2$)]$^{3-/4-}$ agree very well with those found for [Fe(CN)$_6$]$^{3-/4-}$. The value of $\Delta V^\ddagger$ for the studied system is less negative.

The experimental rate constants and activation parameters clearly suggest that oxidation of ascorbate anion by [Fe(CN)$_5$(NO$_2$)]$^{3-}$ follows an outer-sphere electron transfer mechanism. The electron transfer process according to the standard Marcus–Hush model consist of three steps[28] of which the first and the third step (precursor formation and successor dissociation to the reaction products, respectively) are diffusion controlled and the second step involving irreversible electron transfer is rate determining (see Scheme 3). Under conditions where

Table 1 Rate constants and activation parameters for the reduction of [Fe(CN)$_5$(NO$_2$)]$^{3-}$ by ascorbate anion

pH	[H$_2$A]/M	T/°C	P/MPa	k_{obs}/s^{-1}	k/M^{-1} s^{-1}
4.00	0.015	25	0.1	11.3 ± 0.6	
4.20				11.1 ± 0.3	
4.60				19.0 ± 0.6	
4.80				19.4 ± 0.1	
5.05				20.4 ± 0.2	697 ± 7
5.15				21.0 ± 0.1	716 ± 2
5.25				21.0 ± 0.1	716 ± 4
5.30				20.6 ± 0.1	704 ± 4
5.40				21.4 ± 0.1	729 ± 4
5.50				21.3 ± 0.1	728 ± 5
5.60				22.5 ± 0.5	
5.90				23.9 ± 0.3	
6.10				25.1 ± 0.4	
6.40				26.5 ± 0.5	
6.60				29.3 ± 0.2	
6.90				37.2 ± 0.4	
7.00				48.2 ± 0.7	
5.30	0.005	25	0.1	7.0 ± 0.3	645 ± 8
	0.010			12.7 ± 0.1	
	0.015			19.0 ± 0.1	
	0.020			25.3 ± 0.4	
	0.025			32.0 ± 0.5	
5.30	0.015	20	0.1	16.4 ± 0.1	561 ± 3
		25		19.0 ± 0.1	645 ± 8
		30		23.2 ± 0.4	792 ± 12
		35		25.0 ± 0.1	858 ± 2
		40		31.2 ± 0.5	1066 ± 17
5.30	0.005	15	10	7.0 ± 0.4	755 ± 45
			30	7.4 ± 1.1	802 ± 122
			60	8.7 ± 0.4	942 ± 38
			90	9.7 ± 0.3	1050 ± 29
			120	11.0 ± 2.0	1188 ± 211

Table 2 Comparison of the activation parameters for the reduction of cyanoferrate(III) complexes by ascorbate anion at 25 °C

	[Fe(CN)$_6$]$^{3-/4-}$ [a]	[Fe(CN)$_5$(NO$_2$)]$^{3-/4-}$ [b]
k/M^{-1} s^{-1}	842.0 ± 23	645.0 ± 8.0
$\Delta G^\ddagger$/kJ mol^{-1}	56.3	56.5 ± 3.0
$\Delta H^\ddagger$/kJ mol^{-1}	20.8 ± 0.8	21.0 ± 2.0
$\Delta S^\ddagger$/J K^{-1} mol^{-1}	−119.0 ± 3.0	−119.0 ± 6.0
$\Delta V^\ddagger$/cm^3 mol^{-1}	−16.3 ± 4.0	−10.0 ± 0.5

[a] Ref. 3. [b] This work.

$$[Fe(CN)_5(NO_2)]^{3-} + HA^- \underset{}{\overset{K_{os}}{\rightleftharpoons}} \{[Fe(CN)_5(NO_2)]^{3-}\cdot HA^-\} \xrightarrow{k_{et}}$$

$$\{[Fe(CN)_5(NO_2)]^{4-}\cdot HA^{\bullet}\} \rightleftharpoons [Fe(CN)_5(NO_2)]^{4-} + HA^{\bullet}$$

Scheme 3

k_{obs} depends linearly on $[H_2A]_t$ as found in this study, $k = k_{et}K_{os}$ since K_{os} is expected to be small for precursor formation between species with charges of the same sign; K_{os} and k_{et} have to be separated theoretically. The ion-pair formation constant K_{os} can be predicted by using the extended Fuoss equation (6)[29]

$$K_{os} = \tfrac{4}{3}\pi N_A a^3 \exp(-w_{ij}/RT) \tag{6}$$

where a is the contact distance of the ions ($a = r_i + r_j$) and w_{ij} represents the electric work term required to bring the reactants i and j to the contact distance in the precursor complex. The latter term arises from the Debye–Hückel interionic potential to allow for ionic strength effects[29] and is expressed by equation (7) where z_1, z_2 are the charges on the ions, ε_0 the permittivity of

$$w_{12} = z_1 z_2\, e_0^2 N_A / 4\pi\varepsilon_0\varepsilon a(1 + \kappa a) \tag{7}$$

a vacuum, ε the bulk relative permittivity and $\kappa = (2e_0N_AI/\varepsilon_0\varepsilon k_BT)^{\frac{1}{2}}$ with ionic strength I in M. At 25 °C, $I = 0.3$ M and with ionic radii of 0.34 nm for HA^- and 0.44 nm for the $[Fe(CN)_5(NO_2)]^{3-}$ complex [approximated by that of $Fe(CN)_6{}^{3-}$], it follows that $w_{12} = 2.78$ kJ mol^{-1} and $K_{os} = 0.40$ M^{-1}. The value of K_{os} is very small as expected for reactants that are both anions. The calculated value of the electron transfer rate constant $k_{et} = 1.6 \times 10^3$ s^{-1} from $k = k_{et}K_{os}$ is in good agreement with that reported[3] for the related system $[Fe(CN)_6]^{3-}$–HA^-, *viz.* 1.45×10^3 s^{-1}.

The pressure dependence of the rate constant k in accordance with $k = k_{et}K_{os}$ can be expressed as in equation (8) where

$$\Delta V^{\ddagger}_{12} = \Delta V^{\ddagger}_{et} + \Delta \bar{V}_{os} \tag{8}$$

$\Delta V^{\ddagger}_{et}$ represents the mechanistically important term. The value of $\Delta\bar{V}_{os}$ can be evaluated by using the modified version of the Hemmes equation[29] (9) to allow for ionic strength effects. With

$$\Delta\bar{V}_{os} = -RT\left\{\frac{Z_1Z_2e_0^2[\delta + 0.5a\kappa(\delta + \beta)]}{4\pi\varepsilon_0\varepsilon k_BTa(1 + a\kappa)^2} + \beta\right\} \tag{9}$$

$\delta = (\partial\ln\varepsilon/\partial P)_T = 4.64 \times 10^{-4}$ MPa^{-1} (ref. 30) and $\beta = (\partial\ln\varphi/\partial P)_T = 4.67 \times 10^{-4}$ MPa^{-1} (ref. 31), $\Delta\bar{V}_{os} = -3.16$ cm^3 mol^{-1}.

According to the Marcus–Hush–Stranks[32–34] theory the value of the activation volume for the electron transfer step, $\Delta V^{\ddagger}_{et}$, can be evaluated as a sum of calculable contributions, equation (10) where $\Delta V^{\ddagger}_{COUL}$ is the volume change associated

$$\Delta V^{\ddagger}_{et} = \Delta V^{\ddagger}_{COUL} + \Delta V^{\ddagger}_{SR} + \Delta V^{\ddagger}_{DH} + \Delta V^{\ddagger}_{IR} \tag{10}$$

with the rearrangement to bring the ionic species together, expressed by equation (11) [σ is the reactant separation distance

$$\Delta V^{\ddagger}_{COUL} = \frac{N_AZ_1Z_2e_0^2}{4\pi\varepsilon_0\varepsilon\sigma}\left(\frac{\beta}{3} - \delta\right) \tag{11}$$

when the electron is transferred (set to $r_1 + r_2$) (ref. 3)], $\Delta V^{\ddagger}_{SR}$ is the contribution to the rearrangement of the surrounding solvent molecules, expressed by equation (12) [$\varepsilon_{op} = 1.780$ is

$$\Delta V^{\ddagger}_{SR} = \frac{N_Ae_0^2}{16\pi\varepsilon_0}\left[\left(\frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{\sigma}\right)\frac{\partial}{\partial P}\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon}\right)_T - \frac{\beta}{3\sigma}\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon}\right)\right] \tag{12}$$

the relative permittivity of optical frequencies, $\partial(\varepsilon_{op}{}^{-1} - \varepsilon^{-1})_T/\partial P = -1.17 \times 10^{-4}$ MPa^{-1} (ref. 3)], $\Delta V^{\ddagger}_{DH}$ is the term due to the Debye–Hückel or other electrolyte effects, expressed by equation (13) ($a = 0.66$ nm, $B = 3.29$ M$^{-0.5}$, $C = 1.174$ M$^{-0.5}$ are

$$\Delta V^{\ddagger}_{DH} = \frac{RTZ_1Z_2C\sqrt{I}}{(1 + aB\sqrt{I})^2}\,[\delta(3 + 2aB\sqrt{I}) - \beta] \tag{13}$$

the Debye–Hückel parameters[3]) and $\Delta V^{\ddagger}_{IR}$ is the contribution due to internal rearrangement of the two reacting species and is neglected in our calculations since it is usually very small.

From equations (11)–(13) and the quoted values for the necessary parameters it follows that $\Delta V^{\ddagger}_{COUL} = -2.1$, $\Delta V^{\ddagger}_{SR} = -8.0$, and $\Delta V^{\ddagger}_{DH} = +2.0$ cm^3 mol^{-1} such that $\Delta V^{\ddagger}_{et} = -8.1$ cm^3 mol^{-1}. The theoretically evaluated activation volume for the net reaction is $\Delta V^{\ddagger}_{12} = -11.3$ cm^3 mol^{-1}, which is in close agreement with the experimental value $\Delta V^{\ddagger}_{12(exp)} = -10.0 \pm 0.5$ cm^3 mol^{-1}.

The Marcus theory[33] is often used for the estimation of the self-exchange rate constants especially where these are impossible to measure directly. According to this theory, the free energy of activation, $\Delta G^{\ddagger}_{12}$, for a cross-reaction, considering electrostatic effects is given by equations (14)–(16) and $\Delta G^{\ddagger}_{11}$,

$$\Delta G^{\ddagger}_{12} = 0.5\,(\Delta G^{\ddagger}_{11} + \Delta G^{\ddagger}_{22} + \Delta G^{\circ}_{12} + \Delta w) \tag{14}$$

$$\Delta w = w_{12} + w_{21} - w_{11} - w_{22} \tag{15}$$

$$\Delta G^{\circ}_{12} = -nF(E^{\circ}_{11} - E^{\circ}_{22}) \tag{16}$$

$\Delta G^{\ddagger}_{22}$ represent the free energies of activation for the self-exchange reactions. The free energies of activation are determined from the means of the Eyring equation (17). Since the self-

$$k_{ij} = k_BT\,h^{-1}\exp(-\Delta G^{\ddagger}_{ij}/RT) \tag{17}$$

exchange rate constant k_{22} of the couple $HA^{\bullet}$–HA^- has been reported,[3,12] we used the above equations to calculate the self-exchange rate constant k_{11} of the couple $[Fe(CN)_5(NO_2)]^{3-}$–$[Fe(CN)_5(NO_2)]^{4-}$ which was so far unknown.

The free energy change for the cross-reaction ΔG°_{12} is obtained by means of equation (16) using $E^{\circ}_{11} = 0.39$ V (ref. 35) and $E^{\circ}_{22} = 0.71$ V (ref. 3). It results in $\Delta G^{\circ}_{12} = 30.60$ kJ mol^{-1}. The self-exchange rate constant, $k_{22} = 1.6 \times 10^5$ M^{-1} s^{-1} for the couple $HA^{\bullet}$–HA^-, is adopted that leads on the basis of equation (17) to $\Delta G^{\ddagger}_{22} = 43.32$ kJ mol^{-1}. The electric work terms calculated from equation (15) results in $w_{11} = 9.35$ kJ mol^{-1}, $w_{22} = 0$, $w_{12} = 2.78$ kJ mol^{-1}, $w_{21} = 0$ and therefore $\Delta w = -6.57$ kJ mol^{-1}. With the above obtained values of ΔG°_{12}, $\Delta G^{\ddagger}_{22}$, Δw and the experimental value of $\Delta G^{\ddagger}_{12}$, $\Delta G^{\ddagger}_{11} = 46.45$ kJ mol^{-1} and thus $k_{11} = 4.5 \times 10^4$ M^{-1} s^{-1} for the self-exchange rate constant of the couple $[Fe(CN)_5(NO_2)]^{3-}$–$[Fe(CN)_5(NO_2)]^{4-}$ at 25 °C and $I = 0.3$ M. The large value of k_{11} can be ascribed to a low internal reorganization energy required for the self-exchange process, as also found for many other complexes.[12] The obtained value of k_{11} is of the same order of magnitude as those found for the related systems $[Fe(CN)_6]^{3-/4-}$ and $[Fe(C_2O_4)_3]^{3-/4-}$.[3,12]

The experimental rate and activation parameters, as well as the theoretical calculations, clearly suggest that the first step of the reduction of $[Fe(CN)_5(NO_2)]^{3-}$ by ascorbate anion follows an outer-sphere electron transfer mechanism. The theoretical calculations are in perfect agreement with the experimental results and exhibit the same trend as those found earlier for related systems.[3,11,12]

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