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Spin-State Dependence of Heterogeneous Electron-Transfer Rates for the $[Fe^{III}(X\text{-}Sal)_2trien]^+$ Spin-Equilibrium System in Solution

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The heterogeneous electron-transfer rate constants of a series of iron(III) chelates having hexadentate Schiff base ligands, $[(X\text{-}Sal)_2trien]^{2-}$, derived from triethylenetetramine (trien) and various substituted salicylaldehydes (X = H, 3-OCH_3, 5-OCH_3, 3-NO_2, 5-NO_2), have been determined in butyronitrile with 0.1 M TBAP. Previous studies have shown that these compounds exhibit a $^2T \rightleftharpoons {}^6A$ equilibrium in solution and that both the high- and the low-spin forms of the Fe(III) complex are reduced to a high-spin Fe(II) species. Heterogeneous electron-transfer rate constants for the Fe(III) $\rightleftharpoons$ Fe(II) reaction were found to vary between 2.4×10^{-2} and 4.7×10^{-2} cm/s and to depend on the position of the Fe(III) spin equilibrium. A CE mechanism relating the spin equilibrium and the electrochemical reduction is proposed.

In a recent publication we investigated, for the first time, the relationships between thermodynamic potentials for an Fe(III) $\rightleftharpoons$ Fe(II) electrode reaction and a spin-equilibrium process involving Fe(III).[3] The chemical system selected was that derived from triethylenetetramine (trien) and various X-substituted salicylaldehydes (X-Sal) to give $[Fe^{III}(X\text{-}Sal)_2trien]^+$.

The $[Fe^{III}(X\text{-}Sal)_2trien]^+$ cation, whose general structure is shown in Figure 1, has been shown to exhibit $^2T \rightleftharpoons {}^6A$ spin equilibria in both solution and solid state.[4,5] In solution, the population of the high- and low-spin states for the compounds depends upon temperature, solvent, and the X substituent. The dynamics of spin conversion or intersystem crossing for this variable-spin system (eq 1) has also been measured for X =

$$^2T(\text{low spin}, S = {}^1/_2) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} {}^6A(\text{high spin}, S = {}^1/_2) \quad (1)$$

H by laser-Raman *T*-jump[6] and ultrasonic relaxation[7] kinetics, with first-order rate constants for the forward (k_1) and reverse (k_{-1}) reactions being in the range 10^7–10^8 s^{-1}. Since the spin-equilibrium phenomenon apparently has direct relevance to some biological electron-tranfer processes,[8] we have undertaken a detailed electrochemical study of the $[Fe^{III}(X\text{-}Sal)_2trien]^+$ system in solution to determine how the heterogeneous electron-transfer rate constants for this series of compounds depend on the equilibrium position of the thermally populated ^2T and ^6A spin states.

In our earlier study of the same series of compounds,[3] we investigated the redox properties in nine different solvents and reported relationships between the Fe^{III} spin state and thermodynamic half-wave potentials for the Fe(III) $\rightleftharpoons$ Fe(II) reaction. From the temperature dependence of the half-wave potential for the reduction of $[Fe^{III}(X\text{-}Sal)_2trien]^+$ it was possible to measure the electron-transfer entropy change and to relate this to an entropy change associated with the $Fe(III)_{ls} \rightleftharpoons Fe(III)_{hs}$ spin crossover. As part of this study, an Fe(II) derivative was also isolated and characterized as being high spin. However, despite knowledge that the ultimate product is high-spin Fe(II), the actual pathway of electron transfer was not established in our initital study, but it was postulated to proceed by one of two possible pathways. Thus, we are still left with addressing the question as to whether spin crossover occurs before or after electron transfer. This question is more formally posed by reactions 2 and 3, where SC refers to the

$$Fe(III)_{ls}(t_{2g}{}^5) \overset{e^-}{\rightleftharpoons} Fe(II)_{ls}(t_{2g}{}^6) \overset{SC}{\rightleftharpoons} Fe(II)_{hs}(t_{2g}{}^4e_g{}^2) \quad (2)$$

$$Fe(III)_{ls}(t_{2g}{}^5) \overset{SC}{\rightleftharpoons} Fe(III)_{hs}(t_{2g}{}^3e_g{}^2) \overset{e^-}{\rightleftharpoons} Fe(II)_{hs}(t_{2g}{}^4e_g{}^2) \quad (3)$$

spin-crossover process. Reaction 2 involves a chemical reaction (spin crossover) of Fe(II) following electron transfer (EC mechanism), whereas reaction 3 involves an internal chemical reaction of Fe(III) preceding electron transfer (CE mechanism). Of course this analysis assumes that electron transfer between redox species of different spin multiplicities is spin forbidden or, at least, spin restricted, thereby permitting us to exclude the $Fe(III)_{ls}/Fe(II)_{hs}$ and $Fe(III)_{hs}/Fe(II)_{ls}$ couples as possibilities.

In this paper we have extended the thermodynamic aspects of our previous investigation to include a measurement of the heterogeneous electron-transfer rates of the $Fe(III)_{ls,hs} \rightleftharpoons Fe(II)_{hs}$ process. On the basis of these studies we now feel capable of suggesting, with some certainty, the mechanism for this variable-spin electron-transfer reaction.

Experimental Section

Reagent grade *n*-PrCN was treated with concentrated HCl, until the odor of isonitrile was no longer detected, and then dried with K_2CO_3 and fractionally distilled and stored over molecular sieves. *n*-PrCN was made 0.1 M with tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The TBAP was recrystallized from distilled CH_2Cl_2 and dried under reduced pressure. $[Fe(X\text{-}Sal)_2trien]PF_6$ was prepared as described earlier.[3,4]

Cyclic voltammetric measurements were obtained with use of a three-electrode system with a PAR Model 173 potentiostat, a PAR Model 175 Universal programmer, and a Houston Instruments Model 2000 recorder and a storage oscilloscope for fast scan rates. The working electrode was a platinum button, and a platinum wire served as the counterelectrode. A saturated lithium calomel electrode (SLCE) was used as the reference electrode and was separated from the bulk of the solution by a fritted glass bridge. A luggin capillary was employed to reduce *IR* loss. Pictures of traces of fast-scan cyclic voltammograms were taken from an oscilloscopy with a C-5A oscilloscope camera (Tektronix).

Results and Discussion

A typical cyclic voltammogram of $[Fe^{III}(3\text{-}OCH_3\text{-}Sal)_2trien]^+$ at a platinum electrode in *n*-PrCN is shown in Figure 2. No other redox reaction is observed between +1.0 and −1.5 V, and the single one-electron transfer can confidently be assigned as

$$Fe(III) \overset{e^-}{\rightleftharpoons} Fe(II)$$

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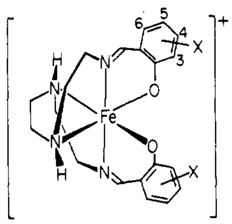

Figure 1. Structure of the $^2T \rightleftarrows {}^6A$ spin-equilibrium cation, $[Fe^{III}(X\text{-}Sal)_2trien]^+$.

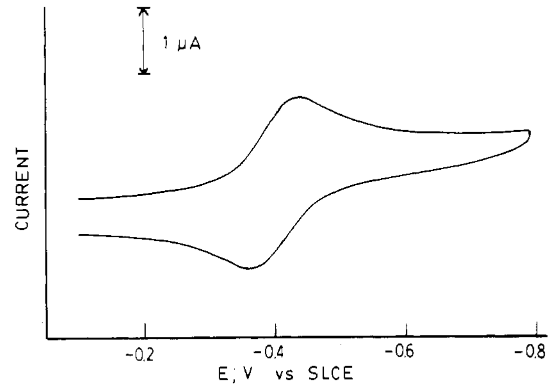

Figure 2. Cyclic voltammogram of 5.0×10^{-4} M $[Fe(3\text{-}OCH_3\text{-}Sal)_2trien]PF_6$ in *n*-PrCN with 0.1 M TBAP at a scan rate of 200 mV/s.

In the same solvent all five complexes of $[Fe^{III}(X\text{-}Sal)_2trien]^+$, where X = $5\text{-}OCH_3$, $3\text{-}OCH_3$, H, $3\text{-}NO_2$, $5\text{-}NO_2$, undergo a reversible, diffusion-controlled one-electron reduction. This behavior has been confirmed in our previous studies on this system using the techniques of cyclic voltammetry, dc polarography, and controlled-potential electrolysis.[3]

For each of the five $[Fe^{III}(X\text{-}Sal)_2trien]^+$ complexes, the separation of the peak potentials was measured as a function of scan rate. Shifts of the peak potentials from the reversible value of 60 mV are considered quasi-reversible, and under these conditions the rate of electron transfer can be calculated from eq 4,[9] where k_s is the heterogeneous electron-transfer rate

$$k_s = \Psi\gamma^{\alpha}\left(\frac{nFv}{RT}D\right)^{1/2} \tag{4}$$

constant (cm/s), n is the number of electrons transferred in each step, v is the potential sweep rate (V/s), D is the diffusion coefficient of the reacting species, $\gamma = (D_o/D_r)^{1/2}$ (where D_o is the diffusion coefficient of the oxidized form of the reactant and D_r is the diffusion coefficient of the reduced form of the reactant), α is the transfer coefficient, and π, F, R, and T have their usual significance. Ψ is related to ΔE_p, the potential difference between the cathodic and anodic peak potentials. Values of Ψ, as defined by eq 4 for various values of ΔE_p, have been tabulated after the solution of the appropriate equations by numerical analysis.[9] Values of diffusion coefficients were calcualted from the Randles–Sevcik equation at slow scan rates and were equal to $7.1 \pm 0.2 \times 10^{-6}$ cm^2/s for all of the complexes investigated in this series. Confirmation that $D_o = D_r$ was obtained from the virtually identical values of i_{pa} and i_{pc}.

Typical data for the determination of the heterogeneous rate constants are shown in Table I. It can be seen that for each complex of the $[Fe^{III}(X\text{-}Sal)_2trien]^+$ series, a constant and self-consistent rate constant is obtained over a scan variation of more than a factor of 10, which is a good indication of the reliability of the rate constants. Here the heterogeneous rate constants are presented to only two significant figures, because of the uncertainty in measuring the trace on the pictures taken from the Polaroid camera to better than 1 or 2 mV.

Table I. Heterogeneous Rate Constant Determination for the Reactions of $[Fe^{III}(X\text{-}Sal)_2trien]^+ + e^- \rightleftarrows [Fe^{II}(X\text{-}Sal)_2trien]$ in *n*-PrCN at 22 °C

substituent, X	scan rate, v, V/s	ΔE, mV	Ψ^a	10^2k_s, cm/s
$5\text{-}OCH_3$	1.0	76	1.50	4.6
	2.0	81	1.13	4.7
	5.0	95	0.68	4.5
	10.0	102	0.52	4.9
				4.7 (av)
$3\text{-}OCH_3$	1.0	77	1.40	4.2
	2.0	85	1.00	4.2
	5.0	99	0.58	3.9
	10.0	114	0.40	3.8
				4.0 (av)
H	1.0	82	1.08	3.2
	2.0	91	0.78	3.3
	5.0	105	0.50	3.3
	10.0	121	0.35	3.3
				3.3 (av)
$3\text{-}NO_2$	1.0	84	1.00	2.9
	2.0	94	0.69	2.9
	5.0	113	0.42	2.8
	10.0	135	0.29	2.7
				2.8 (av)
$5\text{-}NO_2$	1.0	90	0.80	2.4
	2.0	99	0.58	2.4
	5.0	117	0.37	2.5
	10.0	138	0.26	2.4
				2.4 (av)

[a] Taken from ref 9.

Table II. Electron-Transfer Rate Constants for the $[Fe^{III}(X\text{-}Sal)_2trien]^+$ Cations as a Function of Spin Isomer Population at 22 °C

substituent, X	μ_{eff}, $\mu_B{}^a$	% $Fe(III)_{hs}{}^a$	10^2k_s, cm/s^b	$10^2(k_s/\%\ Fe(III)_{hs})$
$5\text{-}OCH_3$	5.59	85	4.7	5.4
$3\text{-}OCH_3$	5.22	73	4.0	5.5
H	5.05	58	3.3	4.7
$3\text{-}NO_2$	4.40	49	2.8	5.7
$5\text{-}NO_2$	3.15	19	2.4	12.6

[a] Taken from ref 4. Measurements were made in acetone.
[b] $[Fe^{III}(X\text{-}Sal)_2trien]^+ + e^- = [Fe^{II}(X\text{-}Sal)_2trien]$. Measurements were made in *n*-PrCN containing 0.1 M TBAP as supporting electrolyte.

Table II gives both the magnetic properties of each complex and a summary of the measured rate constants for the electron-transfer reaction. From this data it is seen that the greater the magnetic moment, or the greater the fraction of the high-spin isomer present in the $Fe^{III}{}_{hs} \rightleftarrows Fe^{III}{}_{ls}$ spin equilibrium, the larger the electron-transfer rate constant and the faster the electron transfer between the redox species and the electrode.

It is known that the reorientation of the solvent molecule, the nature of the supporting electrolyte, ion-pair formation, and change of spin state are factors affecting the change of the activation energy barrier and thus the rate of an electron-transfer reaction.[10-12] (A ligand substituent effect is not taken into consideration because its effect is small in this instance and double-layer corrections due to small changes in the standard potentials of the compounds investigated yield minimal changes in k_s for these solvents.) Since identical solvent, supporting electrolyte, and concentrations were used for all measurements in this study, the iron spin state is the

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most likely factor directly affecting changes in the rate of electron transfer.

According to theory, the heterogeneous electron-transfer rate constant, k_s, is independent of the polarizer concentration.[9] Thus, the concentration dependence of k_s observed in Table II seems to imply that the measured rate of electron transfer is only a conditional rate constant that has incorporated into it rates of both the spin conversion process and the actual heterogeneous electron transfer. This is further implied by the constancy of the term $k_s/\%\ \mathrm{Fe(III)_{hs}}$ for four of the five compounds studied.

The trend of the rate constant increase with the increase in high-spin population strongly points to an overall electron-transfer mechanism that involves a partially rate-determining spin conversion of Fe(III) prior to electron transfer, i.e. reaction 3, and not reaction 2. It is somewhat surprising, however, that the mechanism appears to be identical for all of the complexes of the $[\mathrm{Fe^{III}(X\text{-}Sal)_2trien}]^+$ series. However, this apparent rate-determining spin-conversion step does not seem consistent with the known relative rates of spin crossover and electron transfer measured in these systems, since rate constants for spin conversion are in the range of 10^7–10^8 $\mathrm{s^{-1}}$ in the bulk of solution while those for electron-transfer are 2.4×10^{-2} to 4.7×10^{-2} cm/s. (With the assumption of a reaction-layer thickness of 10 Å this corresponds to an electron-transfer rate constant of 2.4×10^5 to 4.7×10^5 $\mathrm{s^{-1}}$.) Clearly this $\sim 10^5$-$\mathrm{s^{-1}}$ electron-transfer rate is much slower than the measured spin-conversion process, which, therefore, should not be rate determining. For this to be competitive with spin-conversion rates in the bulk of solution, a measured heterogeneous rate constant of 1–10 cm/s would be necessary.

Rates for spin conversion were measured in the absence of supporting electrolyte, and it is possible that the addition of 0.1 M TBAP as supporting electrolyte slows down the rate under our electrochemical conditions. This change, however, should not be large. A more plausible explanation is that the rate of spin conversion is slower at the electrode surface than in the bulk of solution. This decrease in the rate could possibly occur if there were an interaction between the electrical field in the Helmholtz reaction layer and the magnetic field of the diffusing species.[13] Since the data in Table II clearly suggest that spin conversion at the electrode surface is slower than in the bulk of the solution, it is reasonable to conclude that the CE mechanism as shown in reaction 3 is the actual mechanism in the electrochemical reduction of these spin-equilibrium complexes.

In conclusion, it appears from this study that the actual rate of spin conversion may be slowed down at the electrode surface such that the rates become competitive with the heterogeneous electron-transfer rates. If this is generally true, this should enable the electrochemical study of a large number of spin-equilibrium systems in which, at first thought, the spin-conversion rates appear to be too fast for observation by electrochemical methodologies. Several of these systems are now under further investigation.

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Registry No. $[\mathrm{Fe^{III}(5\text{-}OCH_3\text{-}Sal)_2trien}]^+$, 74111-31-2; $[\mathrm{Fe^{III}(3\text{-}OCH_3\text{-}Sal)_2trien}]^+$, 60371-34-8; $[\mathrm{Fe^{III}(Sal)_2trien}]^+$, 60351-91-9; $[\mathrm{Fe^{III}(3\text{-}NO_2\text{-}Sal)_2trien}]^+$, 74111-33-4; $[\mathrm{Fe^{III}(5\text{-}NO_2\text{-}Sal)_2trien}]^+$, 74111-29-8.

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Complex Formation between Iron(III) and Highly Charged Ligands: Equilibria and Reaction Mechanisms

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The kinetics and equilibria of the complexation of iron(III) by the highly charged nonbasic ligands $\mathrm{Fe(CN)_6^{3-}}$, $\mathrm{Co(CN)_6^{3-}}$, and $\mathrm{Mo(CN)_8^{4-}}$ have been investigated in aqueous solution at 25 °C. The stability constants of the 1:1 complexes have been measured and found to be independent of the hydrogen ion concentration but highly sensitive to ionic strength effects. For the system involving octacyanomolybdate ion also a dinuclear complex $\mathrm{Fe_2Mo(CN)_8^{2+}}$ has been detected from both equilibria and kinetics and its stability constant has been measured. This study provides a rather rare example of kinetic evaluation of the equilibrium constants for the formation of outer-sphere complexes from labile aquo ions (K_{os}) and of the ratios between the species associated in the inner-sphere and in the outer-sphere state (K_{is}). The reaction mechanism is discussed in terms of associative interchange and the hypothesis that this mode of activation could be characteristic of all complex formation processes involving tervalent aquo cations is advanced.

Introduction

The basic mechanism for the formation of complexes from solvated cations and ligands is represented in (1), where K_{os}

$$\mathrm{M(H_2O)}_x + \mathrm{L} \overset{K_{os}}{\rightleftharpoons} \mathrm{M(H_2O)}_x,\ \mathrm{L} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{M(H_2O)}_{x-1}\mathrm{L} + \mathrm{H_2O} \quad (1)$$

is an outer-sphere association constant and k_1 is the specific rate at which the ligand changes place with a solvent molecule in the inner coordination shell of the metal ion.[1] k_{-1} is the rate constant for the (reverse) step of aquation.

Provided that the first of the two equilibria in (1) is fast in comparison with the second, the system exhibits only one relaxation time which is given by relationship[2] 2. In most

$$\frac{1}{\tau} = \frac{K_{os}k_1(|\mathrm{M}| + |\mathrm{L}|)}{1 + K_{os}(|\mathrm{M}| + |\mathrm{L}|)} + k_{-1} \quad (2)$$

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