

indication that the mechanism is the same for both processes. In DMF, substitution on Ni^{2+} appears to be going through a 5-coordinate intermediate whereas, in water, substitution proceeds via a concerted process. A more dissociative substitution behavior in DMF than in water has also been noted by Tanaka et al. for Fe^{3+} complexation reactions.²⁶ Steric arguments might be evoked to explain such a trend whereby the change from small water molecules to bulky DMF molecules bonding to the metal cations results in destabilization of solvates of higher coordination number.

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Registry No. DMF, 68-12-2; $\text{Ni}(\text{DMF})_6^{2+}$, 33789-00-3; SCN^- , 302-04-5; diethyldithiocarbamate, 147-84-2.

Supplementary Material Available: First-order rate constants for the formation of NiSCN^+ and $\text{Ni}(\text{Et}_2\text{DTC})_2$ as a function of concentration of reagents and temperature (Table SI) and as a function of pressure (Table SII) (2 pages). Ordering information is given on any current masthead page.

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Solvent and Structure Effects on the Spin-Crossover and Electron-Transfer Properties of $[\text{Fe}^{\text{III}}(\text{X-Salmeen})_2](\text{PF}_6)$ and $[\text{Fe}^{\text{III}}(\text{X-Sal})_2\text{trien}](\text{PF}_6)$ Complexes

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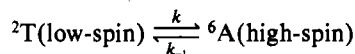
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The electron-transfer reactions for a series of five $[\text{Fe}^{\text{III}}(\text{X-Salmeen})_2](\text{PF}_6)$ and six $[\text{Fe}^{\text{III}}(\text{X-Sal})_2\text{trien}](\text{PF}_6)$ complexes were investigated in nonaqueous media. In the former series, $\text{X} = 3\text{-NO}_2, 5\text{-NO}_2, \text{H}, 4\text{-OCH}_3,$ and 3-OCH_3 . In the latter series, $\text{X} = 3\text{-NO}_2, 5\text{-NO}_2, \text{H}, \text{Cl}, \text{Br},$ and 5-OCH_3 . Both series of $\text{Fe}(\text{III})$ complexes undergo an $\text{Fe}(\text{III})/\text{Fe}(\text{II})$ reaction as well as a low-spin \rightleftharpoons high-spin $\text{Fe}(\text{III})$ spin equilibrium. Each redox reaction was measured as a function of temperature between 220 and 320 K, and the corresponding magnetic moments were recorded in up to seven different nonaqueous solvents. Heterogeneous electron-transfer rate constants, k_e , were also measured at room temperature and correlations made between the position of the spin equilibria and the reversible half-wave potential and/or the electron-transfer rate constant. Correlations were between the substituent constant of the X group and the $E_{1/2}$, k_e , or magnetic moment of each complex as well as between the total entropy of electron transfer and the magnetic moment of $\text{Fe}(\text{III})$ under the same solution conditions. On the basis of these correlations, some attempts were made to determine the factors influencing electron-transfer reactions of spin-equilibria systems.

Introduction

Recent electrochemical studies in our laboratory have focused on how spin equilibria affect the standard redox potentials and electron-transfer rates for oxidation or reduction of $\text{Fe}(\text{III})$,⁴⁻⁶ $\text{Fe}(\text{II})$,⁷ and $\text{Co}(\text{II})$ ⁸ six-coordinate complexes. In the most detailed study of an $\text{Fe}(\text{III})$ spin equilibrium for the $[\text{Fe}^{\text{III}}(\text{X-Sal})_2\text{trien}]^+$ cation, it was illustrated how changes in ligand substituent and the solvent media affected the position of the ${}^2\text{T} \rightleftharpoons {}^6\text{A}$ spin crossover. More importantly, it was illustrated how variable-temperature electrochemistry could be used to investigate the spin-crossover process as it relates to redox potentials and electron-transfer rates.⁵

This work represents a continuation of our studies in this area and incorporates new data for the variable-spin $[\text{Fe}^{\text{III}}(\text{X-Salmeen})_2]^+$ series of complexes shown in Figure 1a for the purpose of comparison with results reported earlier⁵ for the structurally similar $[\text{Fe}^{\text{III}}(\text{X-Sal})_2\text{trien}]^+$ cations (Figure 1b). Both series of six-coordinate iron(III) complexes exhibit



spin equilibria in the solid and solution states with $k_{1,-1} \geq 10^7$

s^{-1} in solution for dynamic spin-crossover processes,⁹⁻¹¹ but the former series are bis(tridentate) species while the latter contain hexadentate ligands.

Experimental Section

Chemicals. $[\text{Fe}^{\text{III}}(\text{X-Sal})_2\text{trien}](\text{PF}_6)$ ($\text{X} = 3\text{-NO}_2, 5\text{-NO}_2, \text{H}, \text{Cl}, \text{Br}, 5\text{-OCH}_3$) and $[\text{Fe}^{\text{III}}(\text{X-Salmeen})_2](\text{PF}_6)$ ($\text{X} = 3\text{-NO}_2, 5\text{-NO}_2, \text{H}, 4\text{-OCH}_3, 3\text{-OCH}_3$) were prepared and characterized as described earlier.^{9,10} Reagent grade methylene chloride (CH_2Cl_2), acetone ($(\text{CH}_3)_2\text{CO}$), dimethylformamide (DMF), *n*-butyronitrile (*n*-PrCN), dimethyl sulfoxide (Me_2SO), and pyridine (py) were purified according to literature methods¹² and stored over molecular sieves prior to use. For the electrochemistry, each solution was made with 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The TBAP was purified by recrystallization from ethyl acetate/ether and dried under reduced pressure.

Instrumentation and Methods. Cyclic voltammetric measurements were obtained with a three-electrode system using either an IBM Model EC 225 voltammetric analyzer or a PAR Model 173 potentiostat and a PAR Model 175 universal programmer coupled with a Houston Instruments Model 2000 recorder or a storage oscilloscope for rapid scan rates. The working electrode was a platinum button, and a platinum wire served as the counterelectrode. A commercial saturated calomel electrode (SCE) or commercial 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 with the same solvent and supporting electrolyte. An SLCE electrode

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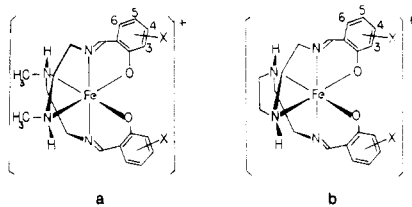


Figure 1. Structures of (a) $[\text{Fe}^{\text{III}}(\text{X-Salmeen})_2]^+$ and (b) $[\text{Fe}(\text{X-Sal})_2\text{trien}]^+$.

is an SCE containing LiCl rather than a KCl filler solution. This difference in the internal filler solution changes the potential such that in aqueous media the SLCE is approximately 60 mV more positive than the SCE. In nonaqueous solutions the potential varies from solvent to solvent. For example, in CH_2Cl_2 the SLCE is approximately 18 mV more negative than the SCE, in acetone it is 100 mV more negative than the SCE, and in pyridine it is 170 mV more negative than the SCE.

Polarographic measurements were made with an EG&G PAR Model 174 polarographic analyzer, utilizing a three-electrode system with a dropping mercury electrode (DME), a platinum wire counterelectrode, and a commercial saturated calomel reference electrode. The current-voltage curves for rapid-scan cyclic voltammograms were taken from an oscilloscope with a Tektronix oscilloscope camera. Measurements of electron-transfer rate constants were obtained by the method of Nicholson using cyclic voltammetry.¹³ Because of the high resistance of some organic solvents, special precautions must be taken when those solvents are used in order to eliminate or minimize potential shifts due to uncompensated iR loss. For this work, a Luggin capillary was employed and positive feedback was utilized. In addition, a small platinum-button electrode (area 0.7 mm²) and low Fe(III) compound concentrations were utilized in order to minimize the peak current and thus the iR loss.

Variable-temperature cyclic voltammetry was performed with an IBM EC 225 voltammetric analyzer with an Omnigraphic 2000 X-Y recorder. A jacketed Brinkman titration vessel was used as the cell, which contained a platinum-wire working electrode and counter-electrode and an SCE reference electrode. The cell was cooled by circulating cold nitrogen gas passed through a heat exchanger that was immersed in a Dewar of liquid nitrogen. The reference electrode was maintained at room temperature throughout the experiment and was separated from the solution by two fritted bridges, each containing the same solvent and supporting electrolyte. The SCE and inner bridge were removed from the cell during cooling. The temperature of the solution was recorded with a thermocouple that was good to ± 1 °C. The cell was allowed to reach a constant temperature before each measurement was taken.

Solution moments of each complex were determined by the Evans method¹⁴ on a Varian A-60A NMR spectrometer. Me_4Si was utilized as the inert reference compound. Pascal's constants were used to correct for ligand diamagnetism.

Results and Discussion

Substituent Effects on the Half-Wave Potentials. The electrochemical reduction of $[\text{Fe}^{\text{III}}(\text{X-Salmeen})_2]^+$ involves a reversible one-electron transfer that may confidently be assigned as an Fe(III)/Fe(II) redox process similar to that reported earlier for the $[\text{Fe}^{\text{III}}(\text{X-Sal})_2\text{trien}]^+$ series.^{5,6} The half-wave potentials for this reduction are shown in Table I and were found to vary between -0.47 and -0.12 V in acetone depending on substituent X. For each Fe(III) complex the peak current dependence on the square root of the scan rate and the invariant peak potential with increasing scan rate (from 20 mV/s to 200 mV/s) are characteristic of a diffusion-controlled, reversible, one-electron transfer.¹⁵ In addition, the peak separation, $E_{\text{pa}} - E_{\text{pc}}$, by cyclic voltammetry was 60 ± 10 mV and polarographic wave analysis plots of E vs. $\log [i/(i_d - i)]$ gave slopes of 60 ± 5 mV, also indicating one-

Table I. Half-Wave Potentials and Magnetic Moments for the $[\text{Fe}^{\text{III}}(\text{X-Salmeen})_2](\text{PF}_6)$ and $[\text{Fe}^{\text{III}}(\text{X-Sal})_2\text{trien}](\text{PF}_6)$ Complexes in Acetone/0.1 M TBAP

substituent X	$2\sigma^a$	$[\text{Fe}^{\text{III}}(\text{X-Salmeen})_2](\text{PF}_6)$		$[\text{Fe}^{\text{III}}(\text{X-Sal})_2\text{trien}](\text{PF}_6)$	
		$E_{1/2}, \text{V}$ (vs. SCE)	$\mu_{\text{eff}}, \mu_{\text{B}}$	$E_{1/2}, \text{V}$ (vs. SCE) ^c	$\mu_{\text{eff}}, \mu_{\text{B}}$
4-OCH ₃	-0.54	-0.47	5.1 ^b		
5-OCH ₃	-0.22			-0.51	5.0
H	0.00	-0.38	4.4	-0.46	4.7
3-OCH ₃	0.24	-0.41	5.3	-0.45	
5-Cl	0.48			-0.39	
5-Br	0.54			-0.36	
3-NO ₂	1.42	-0.15	4.1	-0.17	3.3
5-NO ₂	1.42	-0.12	3.5	-0.14	2.5

^a March, J. "Advanced Organic Chemistry: Reactions, Mechanism, and Structure"; McGraw-Hill: New York, 1977; p 253.

^b Reference 9; measured in the absence of supporting electrolyte.

^c Values of $E_{1/2}$ were measured in V vs. SLCE and converted to V vs. SCE for comparison with other thermodynamic data in this table.

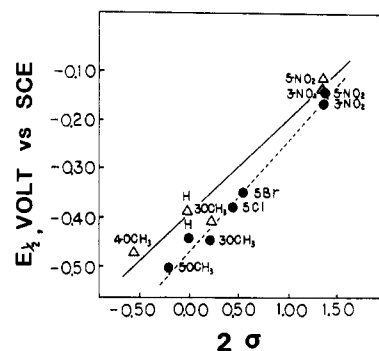


Figure 2. Plot of the half-wave potentials for reduction of $[\text{Fe}^{\text{III}}(\text{X-Salmeen})_2]^+$ (Δ) and $[\text{Fe}^{\text{III}}(\text{X-Sal})_2\text{trien}]^+$ (\bullet) vs. 2σ values in acetone/0.1 M TBAP.

electron-transfer, diffusion-controlled reactions.

Table I also includes a summary of reduction potentials for the $[\text{Fe}^{\text{III}}(\text{X-Sal})_2\text{trien}]^+$ cation in the same solvent and supporting electrolyte. These potentials follow the same trend and dependence on X as the $[\text{Fe}^{\text{III}}(\text{X-Salmeen})_2]^+$ complexes and when reported vs. the SCE reference electrode, are at very similar potentials.

Inspection of Table I indicates that the most positive Fe(III)/Fe(II) reduction potentials are obtained for complexes with NO₂ substituents while the most negative reduction potentials are obtained for complexes containing OCH₃ substituents. A correlation between half-wave potentials and the substituent group is given by the linear free energy relationship¹⁶

$$\Delta E_{1/2} = 2\sigma\rho \quad (1)$$

where σ is the substituent constant representing the sum of the inductive and/or polar effects of all substituents and ρ is the reaction constant, or the parameter indicating the degree to which a given set of substituents influences the electron-transfer process. In this present study 2σ is utilized because there are two substituents per Fe(III) center.

A plot of $E_{1/2}$ vs. 2σ for the $[\text{Fe}^{\text{III}}(\text{X-Salmeen})_2]^+$ and $[\text{Fe}^{\text{III}}(\text{X-Sal})_2\text{trien}]^+$ cations in acetone/0.1 M TBAP is shown in Figure 2. As predicted, Fe(III) complexes containing the electron-donating substituents 4-OCH₃, 5-OCH₃, or 3-OCH₃ are, in general, more difficult to reduce than the unsubstituted

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Table II. Half-Wave Potentials (V vs. SLCE) and Reaction Constants, ρ , for the Fe(III)/Fe(II) Reduction of $[\text{Fe}^{\text{III}}(\text{X-Sal})_2\text{trien}]^+$ in Selected Solvents Containing 0.1 M TBAP

solvent	β^a	ρ , mV ^b	substituent X						
			5-NO ₂	3-NO ₂	H ^c	3-OCH ₃	5-OCH ₃	5-Cl	5-Br
CH ₃ CN ^c	0.31	180	-0.21		-0.49	-0.47	-0.53	-0.40	-0.39
<i>n</i> -PrCN		194	-0.12	-0.13	-0.48	-0.42	-0.46		
Me ₂ SO	0.76	195	-0.11		-0.53		-0.46		
DMF	0.69	200	-0.06		-0.52		-0.42		
CH ₃ COCH ₃	0.48	208	-0.04	-0.07	-0.43	-0.35	-0.41	-0.29	-0.26

^a Taken from ref 19. ^b Calculated from eq 1. ^c Taken from ref 5. Potentials are reported as V vs. SCE.

Table III. Magnetic Moments of the $[\text{Fe}^{\text{III}}(\text{X-Sal})_2\text{trien}](\text{PF}_6)$ Derivatives in Various Solvents Containing 0.1 M TBAP

no.	solvent	β^a	μ_{eff} , μ_B			
			5-NO ₂	3-NO ₂	H	5-OCH ₃
1	CH ₂ Cl ₂	0.00			5.6	5.6
2	CH ₃ CN	0.31			4.8	5.1
3	<i>n</i> -PrCN				4.9	4.6
4	CH ₃ COCH ₃	0.48	2.5	3.3	4.7	5.0
5	py	0.64	2.6	3.5	4.4	4.5
6	DMF	0.69	2.4	3.4	4.1	4.3
7	Me ₂ SO	0.76	2.4	3.1	3.9	4.1

^a Reference 19.

parent complexes. The slopes of the two plots according to eq 1 are 0.14 V for the $[\text{Fe}^{\text{III}}(\text{X-Salmeen})_2]^+$ reduction and 0.18 V for the $[\text{Fe}^{\text{III}}(\text{X-Sal})_2\text{trien}]^+$ reduction. The fact that values of ρ are virtually identical implies that the same electron-transfer mechanism exists not only for each number within the series but also for all the members of both series of complexes.

It is significant to note that a linear relationship between $E_{1/2}$ and 2σ is obtained despite the change of Fe(III) spin-state population from mainly high-spin (OCH₃ substituent) to mainly low-spin (5-NO₂ substituent). This was pointed out in an earlier paper where linear plots between $E_{1/2}$ and σ were also obtained in acetonitrile/0.1 M TBAP.⁵ In this solvent the value of ρ was equal to 0.18 V. Linear relationships between $E_{1/2}$ for reduction of $[\text{Fe}^{\text{III}}(\text{X-Sal})_2\text{trien}]^+$ and σ were also obtained in *n*-PrCN, Me₂SO, and DMF although in these solvents the data are less numerous.

A summary of half-wave potentials for reduction of $[\text{Fe}^{\text{III}}(\text{X-Sal})_2\text{trien}]^+$ in five solvents and a summary of ρ in these same solvents is given in Table II. The fact that linear relations in $E_{1/2}$ are obtained as a function of substituent implies not only that the same mechanism is operative for each member of the series but also that the rate-determining step is independent of the high-spin and low-spin isomer populations. Similar linear relationships between $E_{1/2}$ and 2σ were observed in each solvent as the temperature was varied.⁵ It is also significant to note that an increase in μ_{eff} is associated with a more difficult reduction as seen in Figure 2. This is in contrast to the results of Chant and co-workers,¹⁷ who could not determine a simple relationship between half-wave potential and spin state for spin-equilibrium complexes of the tris(*N,N*-disubstituted dithiocarbamate)Fe(III) class.

The changes of ρ with solvent shown in Table II are not unexpected and have been observed for other systems.¹⁸ The more pertinent effect of solvent on Fe(III) spin state and on Fe(III)/Fe(II) half-wave potentials has been discussed previously^{5,9} in the case of the parent $[\text{Fe}^{\text{III}}(\text{Sal})_2\text{trien}]^+$ complex and is expanded to include other complexes of $[\text{Fe}(\text{X-Sal})_2\text{trien}]^+$ series in the following sections.

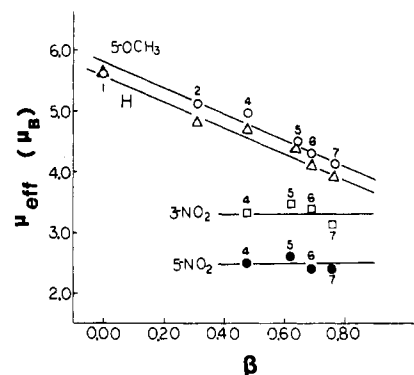


Figure 3. Plot of magnetic moment vs. β for the $[\text{Fe}^{\text{III}}(\text{X-Sal})_2\text{trien}]^+$ cations where X = 5-OCH₃ (○), H (△), 3-NO₂ (□), and 5-NO₂ (●). Numbers correspond to solvents given in Table III.

Solvent Effect on $[\text{Fe}^{\text{III}}(\text{X-Sal})_2\text{trien}]^+$ Spin Equilibria. Seven nonaqueous solvents, varying from CH₂Cl₂ to Me₂SO and py, were used to observe how solvent-solute interactions might affect the position of the spin equilibrium and therefore the magnetic properties of $[\text{Fe}^{\text{III}}(\text{X-Sal})_2\text{trien}]^+$ complexes. Data for the low-spin complexes are unfortunately limited in number (Table III) due to low solubility in "weakly interacting" solvents such as CH₂Cl₂, but in general, results indicate that the magnetic moment is virtually independent of solvent in the case where X = 5-NO₂ and 3-NO₂. In contrast, the nearly high-spin 5-OCH₃ complex shows a significant variation in magnetic moment when a wider range of solvents can be employed. A similar solvent dependency was also noted earlier⁹ for the parent compound in solvents not containing supporting electrolyte, and as shown in Table III, similar trends in μ_{eff} are observed when each solvent contains 0.1 M TBAP. These are the conditions in which the present electrochemical experiments were performed.

Our earlier correlations of magnetic moment with solvents involved plots of μ_{eff} vs. infrared stretching frequencies ($\nu_{\text{N-H}}$ in cm⁻¹)⁹ or μ_{eff} vs. $E_{1/2}$ for the Fe(III)/Fe(II) reduction potentials.⁵ The former plot was reasonably linear while the latter showed a greater degree of scatter. In this present study we have chosen to utilize the solvent parameter β in order to correlate changes in μ_{eff} as a function of changes in solvent. The term β is a value that represents the ability of solvents to hydrogen bond,¹⁹ and this should correlate well with values of magnetic moments measured in different solvents. This indeed is the case as shown in Figure 3. As seen in the figure, a linear relationship exists between μ_{eff} for the $[\text{Fe}^{\text{III}}(5\text{-OCH}_3\text{-Sal})_2\text{trien}]^+$ complexes and the β values (from Table III) for the high-spin complexes. As for the parent compound, it is likely that the major source of this observed solvent dependency in terms of β is related to the strength of hydrogen bonding between the solvent and the amine protons of the trien backbone. In a strongly hydrogen bonding solvent, interactions between the metal complex and solvent would be expected to

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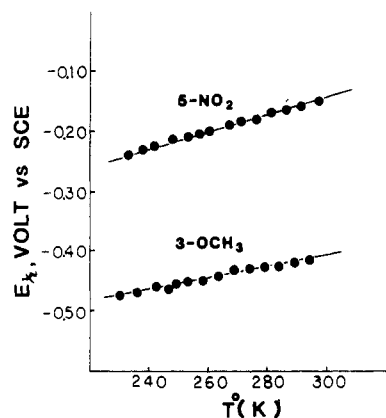


Figure 4. Temperature dependence on the half-wave potentials for the reduction of $[\text{Fe}(\text{X-Salmeen})_2]^+$ in $\text{CH}_3\text{CN}/0.1 \text{ M TBAP}$. Values presented are for $\text{X} = 5\text{-NO}_2$ and 3-OCH_3 . Slopes are given in Table IV.

Table IV. Magnetic Moments and Electron-Transfer Entropy Changes for the Electroreduction of the $[\text{Fe}^{\text{III}}(\text{X-Salmeen})_2]^+$ and $[\text{Fe}^{\text{III}}(\text{X-Sal})_2\text{trien}]^+$ Complexes in $\text{CH}_3\text{CN}/0.1 \text{ M TBAP}$

substituent X	$[\text{Fe}^{\text{III}}(\text{X-Salmeen})_2]^+$			$[\text{Fe}^{\text{III}}(\text{X-Sal})_2\text{trien}]^+$		
	$\mu_{\text{eff}}, \mu_{\text{B}}$ (%hs) ^d	$\Delta E_{1/2}/\Delta T$, mV/K	$\Delta S_{\text{et}},^a$ eu	$\mu_{\text{eff}}, \mu_{\text{B}}$ (%hs)	$\Delta E_{1/2}/\Delta T$, mV/K	$\Delta S_{\text{et}},^a$ eu
3-OCH ₃	5.1 (71.4)	0.91	21.0			
4-OCH ₃		1.02	23.7			
5-OCH ₃				5.1 (71.4)	0.72	16.6
H	4.6 (55.6)	1.13	26.1	4.8 (61.8)	0.84	19.4
3-NO ₂	3.8 (33.9)	1.25	28.8	3.3 (22.4) ^c	0.91	21.0
5-NO ₂	3.4 (24.5)	1.50	34.6	2.5 (7.3) ^c	1.18	27.7

^a Calculated from eq 2. ^b Reference 5; in *n*-PrCN with 0.1 M TBAP. ^c Values measured in acetone with 0.1 M TBAP. ^d %hs denotes the percentage of the complex existing as the high-spin isomer.

increase the crystal or ligand field splitting parameter, Δ , which would thus increase the population of the low-spin isomer.

On the basis of the data in Figure 3 we are able to conclude that, for the high-spin $[\text{Fe}^{\text{III}}(\text{X-Sal})_2\text{trien}]^+$ complexes, hydrogen-bonding effects must also play an important role in determining the high-spin and the low-spin isomer populations. Again, the low-spin complexes show no obvious solvent effect on the spin equilibrium because the low-spin isomer population is already nearly maximized.

Variable-Temperature Electrochemistry. The electrochemical reduction of each $[\text{Fe}(\text{X-Sal})_2\text{trien}]^+$ and $[\text{Fe}(\text{X-Salmeen})_2]^+$ complex was investigated in several solvents as a function of temperature between 220 and 320 K. Nearly linear plots of $E_{1/2}$ vs. T were observed, and from the slope, the entropy change, ΔS_{et} , for the electrochemical reduction may be calculated from the relationship²⁰

$$\Delta S_{\text{et}} = nF(\Delta E_{1/2}/\Delta T) \quad (2)$$

where n is the number of electrons transferred and F is the Faraday constant. Similar plots were also reported for the reduction of the $[\text{Fe}^{\text{III}}(\text{X-Sal})_2\text{trien}]^+$ complexes in *n*-PrCN.⁵ In this solvent values of $\Delta E_{1/2}/\Delta T$ ranged between 0.72 and 1.18 mV/K, which corresponded to a ΔS_{et} of 16.6–27.2 eu.

Figure 4 shows the temperature dependence of $E_{1/2}$ for reduction of the mainly high-spin $[\text{Fe}^{\text{III}}(3\text{-OCH}_3\text{-Salmeen})_2]^+$ complex and the mainly low-spin $[\text{Fe}^{\text{III}}(5\text{-NO}_2\text{-Salmeen})_2]^+$ complex in $\text{CH}_3\text{CN}/0.1 \text{ M TBAP}$. The slopes ($\Delta E_{1/2}/\Delta T$) for $[\text{Fe}^{\text{III}}(3\text{-OCH}_3\text{-Salmeen})_2]^+$ and $[\text{Fe}^{\text{III}}(5\text{-NO}_2\text{-Salmeen})_2]^+$

Table V. Summary of ΔS_{et} (eu) for the $\text{Fe}(\text{III})/\text{Fe}(\text{II})$ Reduction of $[\text{Fe}(\text{X-Sal})_2\text{trien}]^+$ Complexes in Various Solvents Containing 0.1 M TBAP

no.	solvent	β^a	substituent X				
			5-NO ₂	3-NO ₂	H	3-OCH ₃	5-OCH ₃
1	CH_2Cl_2	0.00			5.6	8.9	
2	CH_3CN	0.31			16.7		
3	<i>n</i> -PrCN		27.2	21.0	19.4		16.6
4	CH_3COCH_3	0.48	35.1	32.3	27.9	25.1	28.7
5	py	0.64	33.1		25.0		
6	DMF	0.69	33.3		23.6		24.9
7	Me_2SO	0.76	33.4		30.4		34.9

^a Reference 19.

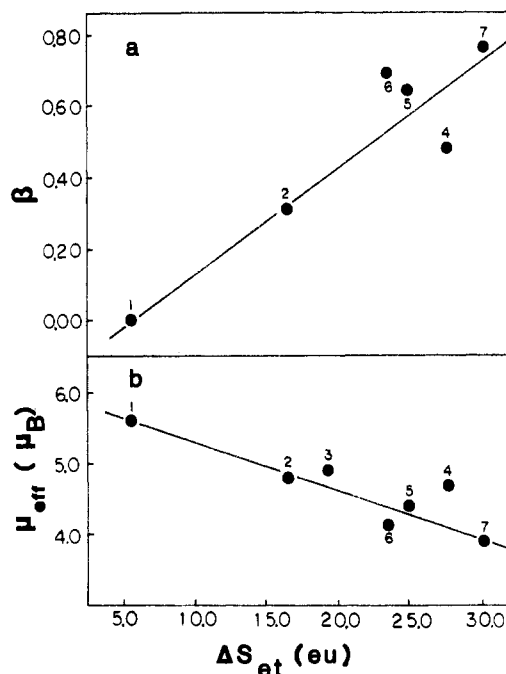


Figure 5. Electron-transfer entropy, ΔS_{et} , vs. the solvent parameter, β , and μ_{eff} . Numbers correspond to solvents given in Table III.

are 0.91 and 1.50 mV/K as determined by least-squares fitting of the data and correspond to electron-transfer entropies of 21.0 and 34.6 eu, respectively. Each of the $[\text{Fe}^{\text{III}}(\text{X-Salmeen})_2]^+$ complexes was investigated by the same method, and ΔS_{et} was found to vary between the values of 21.0 and 34.6 eu. This data is listed in Table IV along with the measured magnetic moments for the $[\text{Fe}(\text{X-Sal})_2\text{trien}]^+$ complexes in $\text{CH}_3\text{CN}/0.1 \text{ M TBAP}$.

From Table IV it can be concluded that the nearly low-spin complexes (5-NO₂, 3-NO₂) have large ΔS_{et} values while the higher spin complexes (3-OCH₃, 4-OCH₃, or 5-OCH₃) have relatively smaller values of ΔS_{et} . This was true for both series of complexes where $\Delta E_{1/2}/\Delta T$ (and ΔS_{et}) decreased in magnitude in direct proportion to an increase in the magnetic moment and therefore to the percent high-spin isomer population.

The temperature dependence of $E_{1/2}$ for reduction of the $[\text{Fe}^{\text{III}}(\text{X-Sal})_2\text{trien}]^+$ complexes was investigated in seven solvent systems. These results are summarized in Table V. As seen in this table, ΔS_{et} values for the $[\text{Fe}^{\text{III}}(\text{Sal})_2\text{trien}]^+$ complexes ranged from 5.6 to 30.4 eu as the solvent was changed from the weakly interacting solvent CH_2Cl_2 to the strongly hydrogen-bonding solvent Me_2SO but decreased from 35.1 eu for the low-spin 5-NO₂ derivative in acetone to 25.1 eu for the high-spin 3-OCH₃ complex in the same solvent. A good correlation of this data is observed from plots of ΔS_{et} vs. both the hydrogen-bonding parameter, β , and the experi-

(20) See for example: Kadish, K. M. *Phys. Bioinorg. Chem. Ser.* **1982**, No. 2, 230.

Table VI. Heterogeneous Electron-Transfer Rate Constants for the Reduction of the $[\text{Fe}^{\text{III}}(\text{X-Salmeen})_2]^+$ Cations as a Function of the Spin Isomer Population at 25 °C in Acetone/0.1 M TBAP

substituent X	$\mu_{\text{eff}}, \mu_{\text{B}}$		%hs ^b	$10^2 k_s$, cm/s
	this work	ref 5 ^a		
3-OCH ₃	5.3	5.4	78.2	6.0
4-OCH ₃	5.1 ^a	5.1	71.4	5.9
H	4.4	5.1	49.9	4.6
3-NO ₂	4.1	3.3	41.6	3.0
5-NO ₂	3.5		26.8	2.0

^a Measured in the absence of supporting electrolyte. ^b Calculated on the assumption that the limiting high-spin (hs) and the limiting low-spin (ls) magnetic moments are 5.9 and 2.0 μ_{B} , respectively.

mentally measured magnetic moment. This is shown in Figure 5, where both relationships are nearly linear.

Electron-Transfer Rate Constants. For each of the $[\text{Fe}^{\text{III}}(\text{X-Salmeen})_2]^+$ complexes, the separation of anodic and cathodic peak potentials was measured as a function of scan rate. In this manner the heterogeneous electron-transfer rate constant can be calculated¹³ from the relationship

$$k_s = \psi \gamma^\alpha \left(\frac{nFvD}{RT} \right)^{1/2} \quad (3)$$

where k_s is the heterogeneous electron-transfer rate 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 and D_r are the diffusion coefficients of the oxidized form and reduced form, respectively), α is the transfer coefficient, and F and RT have their usual significance. The term ψ is related to the potential separation between the cathodic and anodic peak potentials ($E_{\text{pa}} - E_{\text{pc}}$).

Values of k_s for the reduction of $[\text{Fe}^{\text{III}}(\text{Salmeen})_2]^+$ in acetone/0.1 M TBAP were calculated and are summarized in Table VI. Diffusion coefficients used in eq 3 were calculated as 8.2×10^{-6} cm²/s from the Randles-Sevcik equation and were virtually identical for all of the complexes in this series. As seen in Table VI, values of k_s ranged between 2.0×10^{-2} and 6.0×10^{-2} cm/s depending on the nature of the substituent and, therefore, also on the spin state of the complex. The higher the magnetic moment, and thus the high-spin isomer population, the larger the electron-transfer rate constant. This same trend was earlier observed for the reduction of $[\text{Fe}(\text{X-Sal})_2\text{trien}]^+$ in *n*-PrCN.⁵ However, in this case, k_s varied over a somewhat smaller range of 2.4×10^{-2} to 4.7×10^{-2} cm/s. Although there is some scatter in the data, a good correlation does appear to exist between k_s and $E_{1/2}$ for this series of complexes. While it might be expected that the low-spin isomer would be easier to reduce from both a thermodynamic and kinetic point of view, this does not appear to be the case. For example, the 5-NO₂ derivative is the most easily reduced from a thermodynamic point of view but it also appears to exhibit the slowest electron-transfer process. This was also observed for reduction of $[\text{Fe}^{\text{III}}(\text{X-Sal})_2\text{trien}]^+$ and explained on the basis that reduction proceeded in all cases via a high-spin form of Fe(III).⁵ A similar mechanism also seems plausible for the $[\text{Fe}^{\text{III}}(\text{X-Salmeen})_2]^+$ series of variable-spin complexes here.

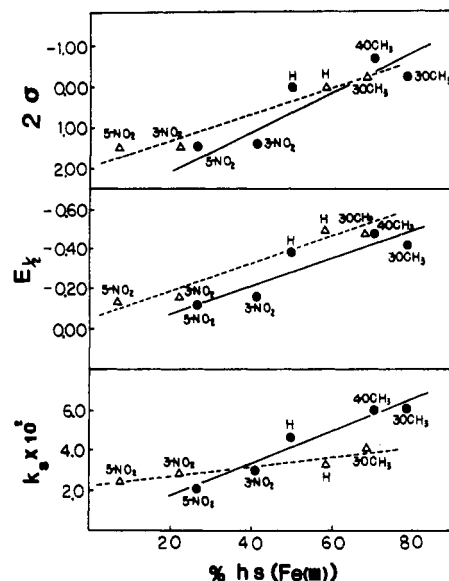


Figure 6. Relationships between 2σ , $E_{1/2}$ (V vs. SCE), and k_s (cm/s) and the (%hs Fe(III)) of the $[\text{Fe}^{\text{III}}(\text{X-Salmeen})_2]^+$ (●) and $[\text{Fe}^{\text{III}}(\text{X-Sal})_2\text{trien}]^+$ (Δ) series of complexes in acetone/0.1 M TBAP.

Summary of Correlations. A summary of data in this study is shown in Figure 6, which displays plots of k_s , $E_{1/2}$, and 2σ vs. the percentage of high-spin Fe(III) isomers for each $[\text{Fe}^{\text{III}}(\text{X-Salmeen})_2]^+$ and $[\text{Fe}^{\text{III}}(\text{X-Sal})_2\text{trien}]^+$ complex. It is important to note here that the spin-conversion process is related to the given substituent constant, which also appears to influence $E_{1/2}$ and k_s . Therefore, the observed correlation between both $E_{1/2}$ and k_s with the percent high-spin Fe(III) may only reflect a substituent effect which is influencing all of the parameters. On the other hand, the correlations between ΔS_{et} and μ_{eff} clearly indicate the possibility that the electron-transfer entropy may be associated with the spin conversion as has been strongly suggested by our previous studies.⁴⁻⁸

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Registry No. $[\text{Fe}^{\text{III}}(4\text{-OCH}_3\text{-Salmeen})_2](\text{PF}_6)$, 65293-74-5; $[\text{Fe}^{\text{III}}(4\text{-OCH}_3\text{-Salmeen})_2]^+$, 65293-73-4; $[\text{Fe}^{\text{III}}(\text{Salmeen})_2](\text{PF}_6)$, 65293-56-3; $[\text{Fe}^{\text{III}}(\text{Salmeen})_2]^+$, 65293-55-2; $[\text{Fe}^{\text{III}}(3\text{-OCH}_3\text{-Salmeen})_2](\text{PF}_6)$, 65293-76-7; $[\text{Fe}^{\text{III}}(3\text{-OCH}_3\text{-Salmeen})_2]^+$, 65293-75-6; $[\text{Fe}^{\text{III}}(3\text{-NO}_2\text{-Salmeen})_2](\text{PF}_6)$, 65293-70-1; $[\text{Fe}^{\text{III}}(3\text{-NO}_2\text{-Salmeen})_2]^+$, 65293-69-8; $[\text{Fe}^{\text{III}}(5\text{-NO}_2\text{-Salmeen})_2](\text{PF}_6)$, 65293-68-7; $[\text{Fe}^{\text{III}}(5\text{-NO}_2\text{-Salmeen})_2]^+$, 65293-67-6; $[\text{Fe}^{\text{III}}(5\text{-OCH}_3\text{-Sal})_2\text{trien}](\text{PF}_6)$, 74111-32-3; $[\text{Fe}^{\text{III}}(5\text{-OCH}_3\text{-Sal})_2\text{trien}]^+$, 74111-31-2; $[\text{Fe}^{\text{III}}(\text{Sal})_2\text{trien}](\text{PF}_6)$, 60351-92-0; $[\text{Fe}^{\text{III}}(\text{Sal})_2\text{trien}]^+$, 60351-91-9; $[\text{Fe}^{\text{III}}(3\text{-OCH}_3\text{-Sal})_2\text{trien}](\text{PF}_6)$, 92344-25-2; $[\text{Fe}^{\text{III}}(3\text{-OCH}_3\text{-Sal})_2\text{trien}]^+$, 92344-01-9; $[\text{Fe}^{\text{III}}(5\text{-Cl-Sal})_2\text{trien}](\text{PF}_6)$, 74050-82-1; $[\text{Fe}^{\text{III}}(5\text{-Cl-Sal})_2\text{trien}]^+$, 74050-81-0; $[\text{Fe}^{\text{III}}(5\text{-Br-Sal})_2\text{trien}](\text{PF}_6)$, 74050-80-9; $[\text{Fe}^{\text{III}}(5\text{-Br-Sal})_2\text{trien}]^+$, 74050-79-6; $[\text{Fe}^{\text{III}}(3\text{-NO}_2\text{-Sal})_2\text{trien}](\text{PF}_6)$, 92269-50-6; $[\text{Fe}^{\text{III}}(3\text{-NO}_2\text{-Sal})_2\text{trien}]^+$, 74111-33-4; $[\text{Fe}^{\text{III}}(5\text{-NO}_2\text{-Sal})_2\text{trien}](\text{PF}_6)$, 74111-30-1; $[\text{Fe}^{\text{III}}(5\text{-NO}_2\text{-Sal})_2\text{trien}]^+$, 74111-29-8.