

enables the decomposition reaction with the formation of propane (eq 2).

On the other hand, however, there is no evidence for the cleavage of the gallium-bromine bond with formation of HBr (eq 3). These results indicate that the bond strengths of the gallium-heteroatom bonds are decreasing in the order of $\text{GaBr}^{13} > \text{GaSe} > \text{GaC}^{14} \sim \text{GaS}$.

The compounds $i\text{-C}_3\text{H}_7(\text{Br})\text{GaEC}_2\text{H}_5$ (E = S, Se) were identified by conventional physical measurements as well as micro-

analyses. The most striking difference in the IR spectra of the chalcogenolates to those of the adducts is the lack of one gallium-carbon stretching frequency. This is, of course, due to the fact that there is only one isopropyl group attached to the gallium atom. An osmometric molecular weight determination in benzene solution reveals a trimeric arrangement of $i\text{-C}_3\text{H}_7(\text{Br})\text{GaSeC}_2\text{H}_5$ in solution.

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Registry No. 1, 122648-93-5; 1-HSC₂H₅, 122700-89-4; 1-HSeC₂H₅, 122700-90-7; GaBr₃, 13450-88-9; (*i*-C₃H₇)₃Ga, 54514-59-9; C₂H₅SH, 75-08-1; *i*-C₃H₇(Br)GaSC₂H₅, 122648-94-6; C₂H₅SeH, 593-69-1; *i*-C₃H₇(Br)GaSeC₂H₅, 122648-95-7.

- (13) Wade, K.; Banister, A. J. In *Comprehensive Inorganic Chemistry*; Bailar, J. C., Emeléus, H. J., Nyholm, R., Trotman-Dickenson, A. F., Eds.; Pergamon Press: Oxford, England, 1973.
 (14) Tuck, D. G. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed., Pergamon Press: Frankfurt/Main, FRG, 1982; Vol. 1, Chapter 7.

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Redox Kinetics of Metal Complexes in Nonaqueous Solutions: Oxidation of Methyl-Substituted Tris(1,10-phenanthroline)iron(II) Complexes by Hexakis(*N,N*-dimethylformamide)iron(III) in Acetonitrile

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Of the methyl-substituted tris(1,10-phenanthroline)iron(II) perchlorates ($\text{Fe}(\text{X-phen})_3^{2+}$), the tetra- and hexamethyl derivatives are quantitatively oxidized by iron(III) in acetonitrile (MeCN) solution, introduced as $\text{Fe}(\text{dmf})_6(\text{ClO}_4)_3$ (dmf = *N,N*-dimethylformamide). For the latter, evidence involving NMR studies is presented for the occurrence of three fast solvation equilibria (L = dmf; coordinated MeCN is omitted), $\text{FeL}_6^{3+} \rightleftharpoons \text{FeL}_3^{3+} + 3\text{L}$. In line with the respective redox potentials, FeL_3^{3+} and FeL_4^{3+} are the redox-active species. At higher [L] only equilibrium positions are reached that are adequately described by the equilibrium $\text{FeL}_4^{3+} + \text{Fe}(\text{X-phen})_3^{2+} \rightleftharpoons \text{FeL}_4^{2+} + \text{Fe}(\text{X-phen})_3^{3+}$. Coupled with the redox equilibrium are the solvation equilibria $\text{FeL}_4^{3+} + e^- \rightleftharpoons \text{FeL}_4^{2+} \rightleftharpoons \text{FeL}_3^{2+} \rightleftharpoons \text{FeL}_2^{2+}$, giving rise to reversible product inhibition at a low concentration level of L. The dependences of the pseudo-first-order redox rate constants are successfully accommodated by a rate law embodying both ion pairing between both reactants and ClO_4^- and ionic strength dependences through work terms for both the free-ion and ion-paired paths. For the iron(III) species also appreciable formation of ion triplets is required. The relationship between the rate constants with no electrostatic interaction and the driving force is shown.

Introduction

In the preceding article² we reported the kinetics of the reduction of $\text{Fe}(\text{phen})_3^{3+}$ by $\text{Fe}(\text{dmf})_6^{2+}$ in acetonitrile (MeCN) with both salts added as the perchlorates. This study faced the problem of a substitutionally labile system complicating an outer-sphere redox process as well as the problem of electrostatic interaction between highly charged reactants in a solvent of moderate dielectric constant and finally the related problem of ion pairing. The analysis of such data represents an awkward problem at the moment owing to the lack of particularly reliable theoretical approaches.

If now methyl groups are introduced into the phenanthroline rings, the redox potential of the iron complex is shifted to more negative values so that the reaction proceeds in the reverse direction, again in MeCN. Thus, upon mixing of an excess of $\text{Fe}(\text{dmf})_6^{3+}$ with tetramethylferroin, quantitative oxidation of the latter is observed.³ The analysis in this earlier paper proved to be erroneous. The correction and the completion of these studies is the purpose of the present paper. In addition, some other methylferroins have been used.

Table I. Redox Potentials^a for $\text{Fe}^{3+/2+}$ in Acetonitrile at 25 °C

complex	$E_{1/2}$, ^b V
$\text{Fe}(\text{dmf})_6^{3+/2+ c}$	1.06 ₈ (100)
$\text{Fe}(\text{dmf})_5(\text{MeCN})^{3+/2+}$	1.27 ^e
$\text{Fe}(\text{dmf})_4(\text{MeCN})_2^{3+/2+}$	1.48 ^d
$\text{Fe}(\text{Me}_6\text{phen})_3^{3+/2+}$	1.52 ₀ (173)
$\text{Fe}(3,4,7,8\text{-Me}_4\text{phen})_3^{3+/2+}$	1.57 ₅ (85)
$\text{Fe}(4,7\text{-Me}_2\text{phen})_3^{3+/2+}$	1.66 ₇ (74)
$\text{Fe}(\text{dmf})_3(\text{MeCN})_3^{3+/2+}$	1.70 ^e
$\text{Fe}(5,6\text{-Me}_2\text{phen})_3^{3+/2+}$	1.76 ₉ (75)
$\text{Fe}(\text{phen})_3^{3+/2+}$	1.83 ₆ (105)
$\text{Fe}(\text{MeCN})_6^{3+/2+ c}$	2.56 ₄ (365)

^a The potentials are referenced to BCr (-1.118 V vs ferrocene/ferrocenium). ^b $E_{1/2}$ taken as $(E_p^{\text{red}} + E_p^{\text{ox}})/2$. Numbers in parentheses are peak separations in millivolts. Scan rate = 100 mV/s, 0.1 M Bu₄N(PF₆) was present, and reactant concentrations were ca. 1 mM. ^c Reference 2. ^d Calculated from the redox equilibrium constant described in the text. ^e Interpolated.

Experimental Section

The ligands 5,6-dimethyl- and 3,4,5,6,7,8-hexamethyl-1,10-phenanthroline (5,6-Me₂phen and Me₆phen) were prepared by Skraup reactions using a literature method.⁴ 4,7-Dimethyl- and 3,4,7,8-tetramethyl-1,10-phenanthroline (4,7-Me₂phen) (Baker) and Me₄phen

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 (2) Schmid, R.; Kirchner, K.; Dickert, F. L. *Inorg. Chem.* 1988, 27, 1530.
 (3) Schmid, R.; Sapunov, V. N.; Gutmann, V. *Ber. Bunsen-Ges. Phys. Chem.* 1976, 80, 1302.

- (4) Calif, G. E.; Samuel, E. L. *Aust. J. Chem.* 1963, 16, 833.

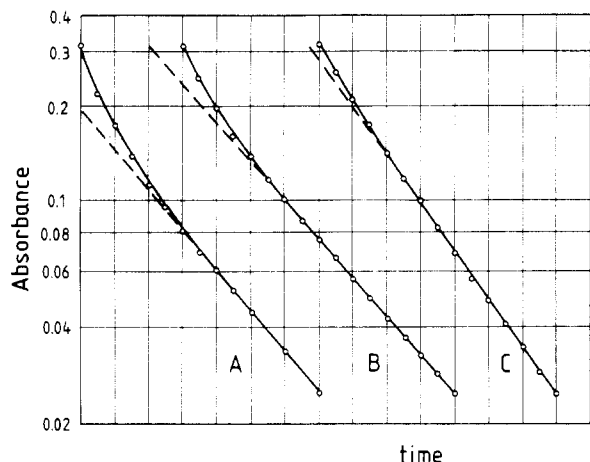


Figure 1. Pseudo-first-order plots for the oxidation of $\text{Fe}(\text{Me}_6\text{phen})_3^{2+}$ (0.1 mM) by $\text{Fe}(\text{III})$ of different millimolar concentrations (time axis in s/division): (A) 0.5 (4), (B) 1 (1.6), (C) 2.5 (0.8). Points are experimental; solid lines are simulations. During the experiments the free dmf concentration increased by 55% (A), 33% (B), and 18% (C), respectively.

(Loba)) were purchased. The perchlorate salts of the corresponding tris(1,10-phenanthroline)iron(II) complexes were made as previously described⁵ and contain 1–2 mol of H_2O , from elemental analyses. $\text{Fe}(\text{dmf})_6(\text{ClO}_4)_3$ ^{3,6} was made, and MeCN and dmf were purified² according to standard methods. Owing to the hazard of metal perchlorates containing organic ligands, the drying temperature was kept below 50 °C, and the solid compounds have not been ground.

The kinetics measurements were done at 25 °C on a Durrum D-110 stopped-flow spectrophotometer as before² by following the consumption of $\text{Fe}(\text{NN})_3^{2+}$ (Me_6phen , λ_{max} 513 nm (ϵ 16 400 $\text{M}^{-1} \text{cm}^{-1}$); Me_4phen , λ_{max} 512 (ϵ 16 000); 4,7- Me_2phen , λ_{max} 513 (ϵ 15 780); 5,6- Me_2phen , λ_{max} 515 (ϵ 14 300)). Occasionally also the formation of $\text{Fe}(\text{NN})_3^{3+}$ (Me_6phen , λ_{max} 660 (ϵ 1220); Me_4phen , λ_{max} 660 (ϵ 1230); 4,7- Me_2phen , λ_{max} 560 (ϵ 1305); 5,6- Me_2phen , λ_{max} 590 (ϵ 957)) was measured with results identical with those of $\text{Fe}(\text{NN})_3^{2+}$ consumption.⁷

The cyclic voltammetric measurements were carried out at 25 °C as before.² The NMR measurements were done on a Nicolet NT200WB instrument at 20 °C. The acquisition parameters were a 4.5- μs pulse width, a 500-ms postacquisition delay, a 20 000-Hz sweep width, a 32K block size, and 256–2048 pulses. Acetonitrile- d_3 was obtained from MSD Isotopes Merck, dried over 4- \AA molecular sieves (activated at about 200 °C under vacuum), degassed by three freeze–pump–thaw cycles, and stored in an evacuated bulb in the dark until used.

Results

Qualitative Observations. Both rate and degree of completion of ferroin oxidation follow the reduction potentials given in Table I. Thus, when excess $\text{Fe}(\text{III})$ was present, only the hexa- and tetramethyl derivatives are quantitatively oxidized. For $\text{Fe}(4,7\text{-Me}_2\text{phen})_3^{2+}$, the reaction reached about 30% completion and was too slow to warrant a kinetic analysis. With $\text{Fe}(5,6\text{-Me}_2\text{phen})_3^{2+}$, finally, as well as with parent $\text{Fe}(\text{phen})_3^{2+}$, there was no detectable reaction.

Oxidation of $\text{Fe}(\text{Me}_6\text{phen})_3^{2+}$. When excess $\text{Fe}(\text{III})$ was present, practically quantitative conversion was ascertained from the absorbance changes. Pseudo-first-order plots deviated from linearity in the initial stages, as is shown in Figure 1; i.e., the initial rates observed were faster than those of the latter part of the reaction. Also seen from Figure 1, this deviation decreased as $[\text{Fe}(\text{III})]$ increased. Further, the deviation decreased when extra dmf was added and the overall rates were dramatically retarded.

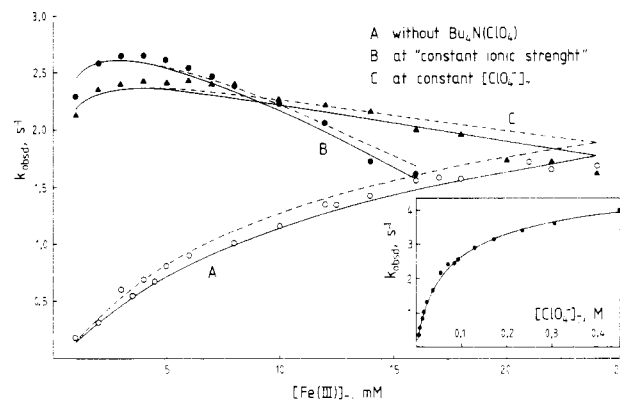


Figure 2. Dependence of the observed rate constant for the oxidation of $\text{Fe}(\text{Me}_6\text{phen})_3^{2+}$ (0.1 mM) on the total iron(III) concentration under various conditions. The inset shows the increase of the rate constant measured for 2 mM $[\text{Fe}(\text{III})]_{\text{T}}$ on the addition of $\text{Bu}_4\text{N}(\text{ClO}_4)$. Points are experimental. The broken curves are calculated by using the full eq 10 and constants given under method a of Table III. The full lines are obtained from eq 10 by using the constants given under method b of Table III, when the terms of e^{6A} , e^{4A} , and e^{3A} are omitted for the FeL_4^{3+} path.

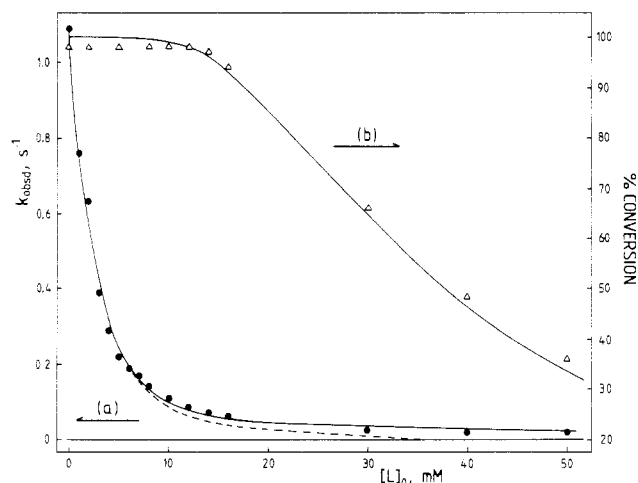


Figure 3. Oxidation of $\text{Fe}(\text{Me}_6\text{phen})_3^{2+}$ (0.1 mM) with $\text{Fe}(\text{III})$ (10 mM): Variation in the observed rate constant (left-hand ordinate) and in the degree of conversion (right-hand ordinate) upon addition of extra dmf. Without adding extra dmf, the conversion is $98 \pm 2\%$. Points are experimental; solid lines are calculations. The broken line was calculated from eq 4.

From 20-fold excess upward the reaction became practically first-order (for at least 4 half-lives). The main kinetic results of this study have been derived from the concentration dependences of the pseudo-first-order rate constants: They were found to increase nonlinearly with $[\text{Fe}(\text{III})]$ when no electrolyte was added and to pass through a maximum when the variation in ionic strength and perchlorate concentration was compensated for by the addition of $\text{Bu}_4\text{N}(\text{ClO}_4)$, respectively (Figure 2). The inset of Figure 2 depicts the dependence of the rate constant on added $\text{Bu}_4\text{N}(\text{ClO}_4)$ at fixed $[\text{Fe}(\text{III})]$. Finally, the rate constants decreased steeply to a limiting value when extra dmf was added (Figure 3). At high [dmf], also shown in Figure 3, the reaction was no longer quantitative. Even in the range of decreasing conversion, the kinetics remained first-order. Also worth noting, the results were independent of whether the dmf was admixed to the $\text{Fe}(\text{III})$ or the ferroin reactant solutions before the reaction.

With ferroin in excess, the reaction was not pseudo-first-order, proceeded to only 70% completion, and was not studied further.

Oxidation of $\text{Fe}(\text{Me}_4\text{phen})_3^{2+}$. Kinetic features were found similar to those described above. The decrease in conversion occurred at concentrations of extra added dmf lower than those in the Me_6phen reaction: At $[\text{Fe}(\text{III})]_{\text{T}} = 10$ mM and $[\text{Fe}(\text{Me}_4\text{phen})_3^{2+}] = 0.1$ mM, the percentage conversions were

(5) Sutin, N.; Gordon, B. M. *J. Am. Chem. Soc.* **1961**, *83*, 70.

(6) Care is necessary in the washing and drying procedures, since the complex seems to be liable to incorporate extra dmf beyond the composition $\text{Fe}(\text{dmf})_6(\text{ClO}_4)_3$. (Cf.: Frederick, F. C.; Johnson, K. E. *J. Inorg. Nucl. Chem.* **1981**, *43*, 1483.) With another sample, obviously not prepared properly, a coordination number for dmf of 4.8 was obtained from NMR spectroscopy instead of 5.7 (10 mM solution in MeCN) (see below).

(7) In the determination of the molar absorptivity coefficients, 2 mol of crystal water was taken into account.

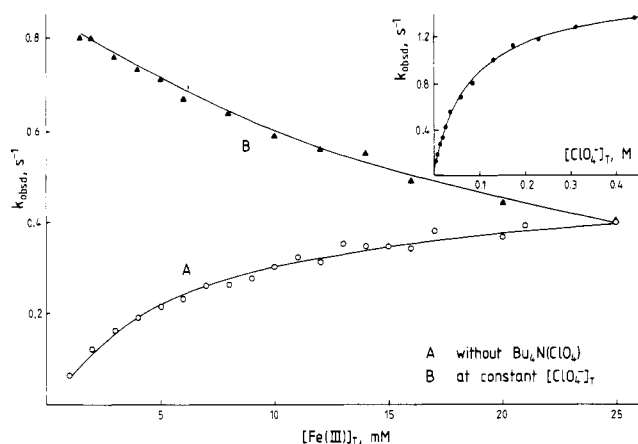


Figure 4. Dependence of the observed rate constant for the oxidation of $\text{Fe}(\text{Me}_6\text{phen})_3^{2+}$ (0.1 mM) on the total iron(III) concentration under two different conditions. The inset shows the increase of the rate constant measured for 2 mM $[\text{Fe}(\text{III})]_T$ on the addition of $\text{Bu}_4\text{N}(\text{ClO}_4)$. Points are experimental. The solid curves are fits to eq 10, independent of the modifications applied.

Table II. Numbers, n_{dmf} , of Dimethylformamide Molecules Coordinated at Iron(III) in Solutions of $\text{Fe}(\text{dmf})_6(\text{ClO}_4)_3$ in MeCN

$[\text{Fe}(\text{III})]_T$, mM	NMR ^a	n_{dmf}		
		kinetics		
		method a ^b	method b ^c	method c ^d
1.70	5.19	5.25	5.44	5.76
3.03	5.32	5.45	5.55	5.81
8.60	5.72	5.69	5.71	5.88
76.50	5.89	5.90	5.89	5.96

^a Uncertainty ± 0.20 . ^b Calculated from the β values derived from the three-equilibrium system with $\beta_1 = 6 \times 10^{-4}$ M, $\beta_2 = 5 \times 10^{-7}$ M², and $\beta_3 = 2 \times 10^{-10}$ M³. ^c Calculated from a rate law involving two solvation equilibria with $\beta_1 = 9 \times 10^{-4}$ M and $\beta_2 = 8.7 \times 10^{-8}$ M². ^d Calculated from a rate law with a single equilibrium where $\beta_1 = 1.32 \times 10^{-4}$ M.

(millimolar amount of extra added dmf in parentheses) 98 (8), 96 (9), 90 (10), and 80 (12). Further, Figure 4 displays the concentration dependences of the observed rate constant on both $[\text{Fe}(\text{III})]$ and $\text{Bu}_4\text{N}(\text{ClO}_4)$.

Speciation of Fe(III). As in the preceding paper,² the speciation was studied by NMR spectroscopy. At room temperature, separate resonances of coordinated and bulk dmf could be detected in the ¹H NMR spectrum of $\text{Fe}(\text{dmf})_6(\text{ClO}_4)_3$ dissolved in CD_3CN . The mole fraction of coordinated dmf was calculated from the ratio of the area of the two peaks between 20 and 100 ppm (assigned to the methyl protons cis and trans, respectively, to the oxygen atom of coordinated dmf) and the area of the signal at 8 ppm assigned to the formyl resonance of free dmf, whereas that of coordinated dmf could not be detected, as expected. The signal of the residual protons of CD_3CN has been used as reference for the shifts. The coordination numbers of dmf thus obtained for various $[\text{Fe}(\text{III})]$ are given in the first row of Table II.

Discussion

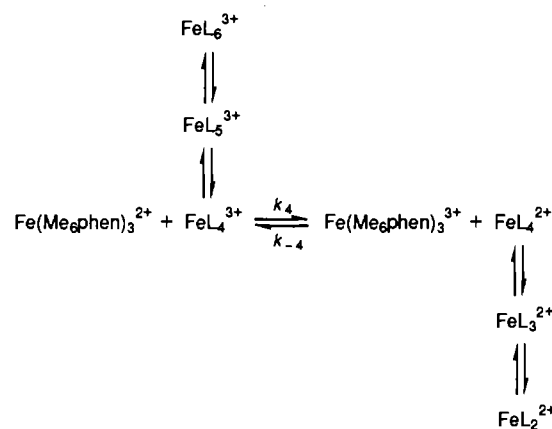
Oxidation of $\text{Fe}(\text{Me}_6\text{phen})_3^{2+}$. The decrease in the pseudo-first-order rate constant when extra dmf is added (Figure 3) is found to be independent of the mode of addition of dmf (i.e. either to the ferriox or iron(III) solution), and this strongly suggests the existence of solvation equilibria, involving the iron(III) center, that are fast compared to the redox process. The large effect of small additions of dmf would further suggest that not much dmf is lost from $\text{Fe}(\text{dmf})_6^{3+}$ dissolved in MeCN. This is in accordance with the NMR measurements pointing to a mean number of coordinated dmf molecules, n_{dmf} , equal to about 5.7 for 10 mM $[\text{Fe}(\text{III})]$ used to generate Figure 3. From the considerations of the variations of both k_{obsd} with $[\text{dmf}]$ (within the 100% conversion range) and n_{dmf} with the total iron(III) concentration, given by NMR spectroscopy, a reaction scheme is proposed featuring three

Table III. Summary of Equilibrium and Kinetic Parameters Obtained from the Various Concentration Dependences at 25 °C

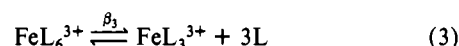
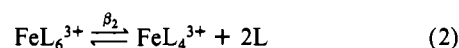
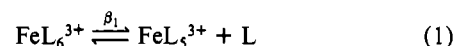
Equilibrium Constants				
β_1 , M (eq 1)	$(6 \pm 3) \times 10^{-4}$	K_1 , M ⁻¹ (eq 7)	110 \pm 10	
β_2 , M ² (eq 2)	$(5 \pm 3) \times 10^{-7}$	K_2 , M ⁻¹ (eq 8)	75 \pm 10	
β_3 , M ³ (eq 3)	$(2 \pm 1) \times 10^{-10}$	K_3 , M ⁻¹ (eq 9)	3 \pm 1	
Rate Constants (M ⁻¹ s ⁻¹) with No Electrostatic Work				
	method a ^a	method b ^b	method c ^c	
Me_6phen	k_3	3.87×10^4	3.89×10^4	
	k_4	5.95×10^3	6.18×10^3	
	k_{-4}	2.80×10^4	2.91×10^4	
Me_4phen	k_3	1.91×10^4	1.90×10^4	1.85×10^4
	k_4	2.39×10^2	2.92×10^2	1.85×10^3
	k_{-4}	1.05×10^4	1.29×10^4	8.18×10^4

^a Calculated by using the full eq 10. ^b Calculated by using eq 10 but omitting, for the FeL_4^{3+} path, the terms of e^{6A} , e^{4A} , and e^{3A} . ^c Calculated by using eq 10 as in method b^b with additionally the omission of the term of e^{2A} for the FeL_4^{3+} path. (This alternative was unsuccessful for the Me_6phen case.)

Scheme I



solvation equilibria (in the following, dmf is denoted as L and coordinated MeCN is omitted) with both FeL_3^{3+} and FeL_4^{3+} being redox-active:



The expression for the rate constant for this mechanism, for $[\text{Fe}(\text{III})]$ taken in large excess, is given by eq 4 ($[\text{Fe}(\text{III})]_T$ is the total

$$k_{\text{obsd}} = \frac{(k_3^* \beta_3 + k_4^* \beta_2 [\text{L}]) [\text{Fe}(\text{III})]_T}{[\text{L}]^3 + \beta_1 [\text{L}]^2 + \beta_2 [\text{L}] + \beta_3} \quad (4)$$

iron(III) concentration), where k_3^* and k_4^* are the rate constants of reduction of FeL_3^{3+} and FeL_4^{3+} , respectively, at the particular ionic strength and counterion concentration present.⁸ The set of β values that accounts for both eq 4 (left-hand curve in Figure 3) and the NMR data (under method a in Table II) is listed in Table III.⁹

(8) When the kinetic data were fit to eq 4, the free dmf concentration was supplied from the roots of the material balance equation through Newton's method, $[\text{L}]^4 + [\text{L}]^3 \{\beta_1 - [\text{L}]_0\} + [\text{L}]^2 \{\beta_2 - \beta_1([\text{L}]_0 + [\text{Fe}(\text{III})]_T)\} + [\text{L}] \{\beta_3 - \beta_2([\text{L}]_0 + 2[\text{Fe}(\text{III})]_T)\} - \beta_3([\text{L}]_0 + 3[\text{Fe}(\text{III})]_T) = 0$, derived from the material balance equations $[\text{Fe}(\text{III})]_T = [\text{FeL}_6^{3+}] + [\text{FeL}_5^{3+}] + [\text{FeL}_4^{3+}] + [\text{FeL}_3^{3+}]$ and $[\text{L}] - [\text{L}]_0 = [\text{FeL}_5^{3+}] + 2[\text{FeL}_4^{3+}] + 3[\text{FeL}_3^{3+}]$.

(9) It may be mentioned that the decrease with $[\text{L}]$ of k_{obsd} can also adequately be described by two solvation equilibria with FeL_4^{3+} reacting or even by a single equilibrium with FeL_3^{3+} reacting. In both cases, however, the coordination numbers calculated for the low iron(III) concentrations are too high (Table II).

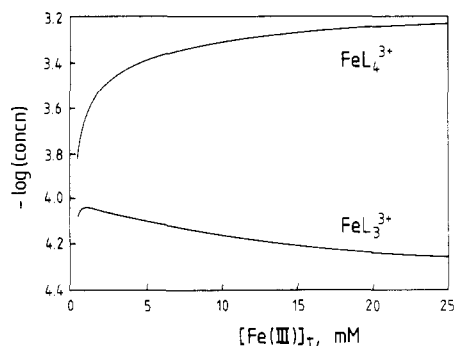
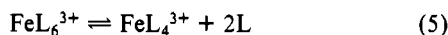
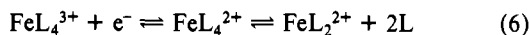


Figure 5. Plots of $-\log$ of the concentrations of the reactive species present in solution vs the total iron(III) concentration, derived from the β values given in Table III.

The S-shaped decrease in conversion at higher $[L]$ depicted by the right-hand curve in Figure 3 is well described by Scheme I. Evidence for a genuine reversible redox reaction is provided by the fact that the results could be reproduced when the reaction is carried out in the opposite direction, namely starting with a mixture without added extra dmf. On the basis of the speciations for both Fe(III) and Fe(II), the latter being known from the previous study,¹⁰ the essential solvation equilibria are



and



From the decrease in conversion when dmf is added, the equilibrium constant $K = k_4/k_{-4}$ is calculated¹¹ to be 0.213 ± 0.006 . The right-hand full curve in Figure 3 is drawn by using this value. Hence, $E = -40$ mV. From $E_{1/2}$ for hexamethylferroin in Table I, then, $E_{1/2}(\text{FeL}_4^{3+/2+}) = 1.48$ V, which may be compared to the value of 1.57 V, interpolated by taking the reduction potential as a linear function of the dmf and MeCN ligands.

Simulations obtained by numerical integration of the differential equations arising from Scheme I satisfactorily reproduced the following kinetic features: (i) Deviations arise from pseudo-first-order behavior in the initial stages for the case of no dmf added and only a 5–20-fold excess of Fe(III) over the ferroin reactant. This is due to an increase in the free dmf concentration during the reactions, i.e. the occurrence of (reversible) product inhibition (see caption to Figure 1). (ii) In the range of decreasing conversion, slight deviations from a pseudo-first-order rate law appear in the initial stages, but after less than 0.5 half-life the reactions are practically first-order.¹² This is interesting, since

(10) From ref 2, $[\text{FeL}_4^{2+}] = \beta_4'[\text{L}]^2[\text{Fe(II)}]_{\text{T}} / (1 + \beta_1'[\text{L}] + \beta_2'[\text{L}]^2 + \beta_3'[\text{L}]^3)$, where $\beta_1' = 0.34 \text{ M}^{-1}$, $\beta_2' = 10.48 \text{ M}^{-2}$, and $\beta_3' = 2.24 \text{ M}^{-3}$.

(11) With the material balance equations $[\text{Fe}(\text{Me}_6\text{phen})_3^{2+}]_0 = [\text{Fe}(\text{Me}_6\text{phen})_3^{2+}] + [\text{Fe}(\text{Me}_6\text{phen})_3^{3+}]$ and $[\text{Fe}(\text{Me}_6\text{phen})_3^{3+}] = [\text{Fe(II)}]_{\text{T}}$, the quadratic dependence of the product concentration ($[\text{Fe}(\text{Me}_6\text{phen})_3^{3+}] = x$) on $[L]$ is derived as $ax^2 + bx + c = 0$, with $a = \beta_4'[\text{L}]^2 + \beta_3'[\text{L}]^3$, $b = K\beta_3'[\text{Fe(III)}]_{\text{T}}(1 + \beta_1'[\text{L}] + \beta_2'[\text{L}]^2 + \beta_3'[\text{L}]^3)$, and $c = -b[\text{Fe}(\text{Me}_6\text{phen})_3^{2+}]_0$. Since $[\text{Fe(III)}]_{\text{T}} \gg [\text{Fe(II)}]_{\text{T}}$, $[L]$ is given by the material balance equation given in ref 8. Measured values of $[\text{Fe}(\text{Me}_6\text{phen})_3^{3+}]$ were fitted to the solutions of the quadratic equation with $[L]$ taken as independent variable, and K and the β 's as floating and constant parameters, respectively. In taxing the reliability of the obtained value of $K = 0.213$, we also take into consideration the equilibrium $[\text{Fe}(\text{Me}_6\text{phen})_3^{2+}] + [\text{FeL}_4^{3+}] + [L] = [\text{Fe}(\text{Me}_6\text{phen})_3^{3+}] + [\text{FeL}_2^{2+}]$, which would have the same polynomial in $[L]$ in the mass balance equations and actually leads to the same equations as above with the only difference that, in a , β_4' is to be replaced by β_3' . With the 22-fold reactivity of FeL_4^{2+} over that of FeL_2^{2+} and the speciation of Fe(II), at $[\text{Fe(II)}]_{\text{T}} = 0.1$ mM and $[\text{dmf}]_0 = 30$ mM, as $[\text{FeL}_4^{2+}] = 9.5 \times 10^{-4}$ mM and $[\text{FeL}_2^{2+}] = 6 \times 10^{-6}$ mM, the FeL_4^{2+} path would contribute 14.3% to the measured degree of conversion.

(12) The pseudo-first-order rate constants obtained from the initial, middle, and final parts, respectively, of the simulated and logarithmized curves are 0.022, 0.025, 0.027 s^{-1} (30 mM $[L]_0$), 0.019, 0.023, 0.025 (40 mM), and 0.017, 0.021, 0.024 (50 mM). Note that the insensitivity of k to variation in $[L]_0$ is correctly simulated.

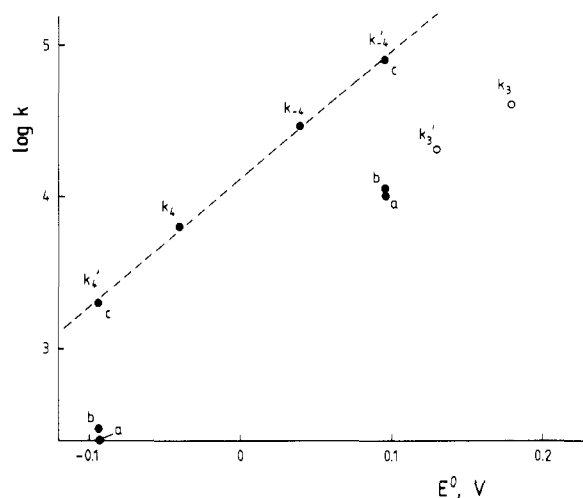
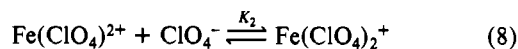
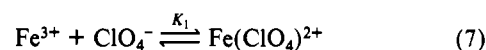


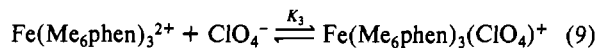
Figure 6. The dependence of the redox rate constants with no electrostatic work on the driving force. The dashed line represents the limiting relation $\Delta \log k = 8.47E$. For a , b , and c , see methods a–c in Table III. The primed constants are for the Me_6phen reaction.

the reverse reaction is second-order with equal concentrations of the two reactants.

With the inner-sphere speciation established, the concentration dependences of Figure 2 can be analyzed. For the occurrence of a maximum in the $[\text{Fe(II)}]_{\text{T}}$ dependence of k_{obsd} when ionic strength and counterion effects are minimized, the speciation diagram presented in Figure 5 is pertinent showing that $[\text{FeL}_3^{3+}]$ and $[\text{FeL}_4^{3+}]$ are decreased and increased, respectively, when $[\text{Fe(III)}]_{\text{T}}$ is increased. The difference between curves B and C of Figure 2, in addition, would point to a strong effect of perchlorate. Within the results of the preceding study,² the following reaction model led to a gratifying description of all the experimental results: Iron(III) forms ion pairs and ion triplets with perchlorate



These equilibria are taken to be species-invariant, Fe^{3+} denoting any Fe(III) species present in solution. Slight ion pairing is also expected for the ferroin reactant



Therefore, six reaction paths for each solvate species must be considered. In addition, each reaction path is ionic strength dependent through electrostatic work. Compared to that, the solvation equilibria are assumed to be unaffected by ionic strength. To further reduce the number of parameters to be adjusted, the approximation was chosen that ion pairing does not affect the rate constant with no electrostatic interaction. This point will be addressed further in the next section. The resulting expression for the rate constant is given by the following ($X = \text{ClO}_4^-$):

$$k_{\text{obsd}} = Q \frac{(\beta_3 k_3 + \beta_2 k_4 [L]) [\text{Fe(III)}]_{\text{T}}}{[L]^3 + \beta_1 [L]^2 + \beta_2 [L] + \beta_3} \quad (10a)$$

where

$$Q = \frac{(e^{6A}) + K_1[X](e^{4A}) + K_3[X](e^{3A}) + K_1 K_2 [X]^2 (e^{2A})}{(1 + K_3[X])(1 + K_1[X] + K_1 K_2 [X]^2) + \frac{K_1 K_3 [X]^2 (e^{2A}) + K_1 K_2 K_3 [X]^3 (e^A)}{(1 + K_3[X])(1 + K_1[X] + K_1 K_2 [X]^2)}} \quad (10b)$$

and²

$$A = \frac{7.12I^{1/2}}{1 + 0.48rI^{1/2}} - \frac{15}{r} \quad (10c)$$

Thus, both k_3 and k_4 in eq 10a refer to infinite ionic strength.¹³ The agreement with experiment using eq 10 and the constants listed in Table III is shown by the broken curves of Figure 2.¹⁵ Further, from K and k_4 , a value for k_{-4} is provided, also given in Table III.

An appreciable improvement (full curves of Figure 2) is obtained when the FeL_4^{3+} ion is allowed to be redox-active in precursor complexes only having at least two perchlorate ions attached, i.e. admitting only the terms of e^{2A} and e^A in eq 10b.¹⁶ The values for k_3 and k_4 obtained in this way are only slightly different from the above ones (Table III). The relationship to the driving force is shown in Figure 6.

Oxidation of $\text{Fe}(\text{Me}_6\text{phen})_3^{2+}$. The decrease in conversion when dmf is added was successfully treated in the same way as above, yielding the equilibrium constant of $K = (2.26 \pm 0.09) \times 10^{-2}$ and hence $E = -97$ mV. The difference between this and the above value of -40 mV is just the potential difference between the two phen complexes (Table I), confirming that the same equilibrium is dealt with in both systems. Further, a comparison of the Figures 4 and 2 reveals a stronger decrease in k_{obsd} with $[\text{Fe}(\text{III})]_{\text{T}}$ under the condition of constant perchlorate concentration in the Me_4phen case. On the basis of eq 10 this can be interpreted in two alternative ways. (i) If all ionic species present of both FeL_3^{3+} and FeL_4^{3+} do react, a larger k_3/k_4 ratio is required for the Me_4phen reaction. Thus, application of the full eq 10 to the experimental data of Figure 4 gives a k_3/k_4 ratio of 80 compared to 6.5 calculated for the Me_6phen case. As a consequence, the values for k_4 and k_{-4} calculated for the Me_4phen reaction do not fit on the linear free energy relationship (LFER) for the Me_6phen analogue (see, in Figure 6, the large deviations of points a from the broken line representing the limiting relation $\Delta \log k = 8.47E$). (ii) Not all ionic species of FeL_4^{3+} are kinetically active. There is no significant improvement, however, when the terms of e^{6A} , e^{4A} , and e^{3A} are omitted, as done above (see points b in Figure 6, giving a k_3/k_4 ratio of 65). When, finally, also the

term of e^{2A} was dropped, i.e. allowing FeL_4^{3+} to react only within the $\text{FeL}_4\text{Fe}(\text{Me}_4\text{phen})_3(\text{ClO}_4)_3^{2+}$ aggregate, the calculated rate constants fall on the line (points c in Figure 6). In this case the k_3/k_4 ratio is equal to 10, comparable with the value of 6.5 obtained for the Me_6phen reaction. It should be noted that the three modifications of eq 10 yield the same good fits to experiment (full curves of Figure 4). All the rate constants calculated with the various assumptions are summarized in Table III.

Concluding Remarks

The excellence of the fits in all cases supports our reaction model and would lend support to the reasonability of the assumptions included. One point that is somewhat clouding our satisfaction concerns the ion-pairing equilibrium constants taken as independent of ionic strength. However, as in our earlier study,² pertinent attempts using Debye-Hückel activity coefficients in addition to ionic strength dependent rate constants, through work terms, proved to be unsuccessful. Actually, we are not aware of any case reported where, in an ion-pairing rate expression of the type $k_{\text{obsd}} = (k_0 + k_1 K_{\text{assn}}[\text{X}^-]) / (1 + K_{\text{assn}}[\text{X}^-])$, rate and equilibrium parameters both were treated as varying with ionic strength. To date, as far as we know, ionic strength variant ion-pairing equilibrium constants have been accommodated within reaction systems only in which one of the reactants is uncharged, i.e. in which there is no electrostatic work required to form the precursor complex.^{18,19} However, as the authors noted, the data were also fit well without activity coefficients included.²⁰

A related problem concerns the significance of the k_0/k_1 ratio in the above equation in that it strongly depends on the other assumptions made in deriving the rate law considered (e.g., whether or not activity coefficients, electrolyte association, etc. are included). Whereas the salt dependence of the rate of oxidation of ferrocene by some cobalt clathrochelates in tetrafluoroborate medium suggests that ion association decreases electron-transfer rates,^{18,19} the rate of oxidation of ferrocene by $\text{Fe}(\text{dmf})_6^{3+}$ in $\text{MeCN}/\text{ClO}_4^-$ medium is very little affected by $\text{Bu}_4\text{N}(\text{ClO}_4)$ (added up to 0.1 M).²¹ In the case that both reactants are charged as in the oxidation of $\text{Fe}(\text{dmf})_4(\text{MeCN})_2^{2+}$ by $\text{Fe}(\text{phen})_3^{3+}$ in $\text{MeCN}/\text{ClO}_4^-$ medium, we have found that within the ion-pairing formalism the ionic strength effect is concisely described by work terms. For this condition the result of the fitting procedure was $k_1 > k_0$ by about a factor of 2, but k_1 approached k_0 if partial association of $\text{Bu}_4\text{N}(\text{ClO}_4)$ was included.² Thus, we started with the assumption of $k_0 = k_1$ in order to reduce the number of adjustable parameters. This approach was surprisingly successful. The result gives us some evidence that ion pairing in the present systems can be interpreted as predominantly contributing to the electrostatic work needed to bring the reactants together. Compared to that, a possible effect on electron-transfer reactivity cannot be resolved.

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Registry No. $\text{Fe}(\text{Me}_6\text{phen})_3^{2+}$, 17378-70-0; $\text{Fe}(\text{Me}_6\text{phen})_3^{2+}$, 23555-66-0; $\text{Fe}(\text{dmf})_6^{3+}$, 21750-26-5.

- (13) In application of eq 10, the free perchlorate concentration was calculated from the roots of the material balance (calculated by Newton's method), $[\text{X}]^3\{K_1K_2\} + [\text{X}]^2\{K_1 - K_1K_2([\text{Fe}(\text{III})]_{\text{T}} + [\text{S}])\} + [\text{X}]\{1 - K_1(2[\text{Fe}(\text{III})]_{\text{T}} + [\text{S}])\} - (3[\text{Fe}(\text{III})]_{\text{T}} + [\text{S}]) = 0$, where S denotes the $\text{Bu}_4\text{N}(\text{ClO}_4)$ added. This equation is derived from the material balance equations (a) $[\text{Fe}(\text{III})]_{\text{T}} = [\text{Fe}^{3+}] + [\text{FeX}^{2+}] + [\text{FeX}_2^{+}]$, (b) $[\text{X}]_{\text{T}} = [\text{X}] + [\text{FeX}^{2+}] + 2[\text{FeX}_2^{+}]$, and (c) $[\text{X}]_{\text{T}} = 3[\text{Fe}(\text{III})]_{\text{T}} + \text{S}$. With $[\text{X}]$ given, the ionic strength is calculated from $I = 0.5(9[\text{Fe}^{3+}] + 4[\text{FeX}^{2+}] + [\text{FeX}_2^{+}] + [\text{X}] + [\text{S}])$. In the treatment, at first the salt dependence of k_{obsd} was fitted by means of a nonlinear least-squares program with only K_1 , K_2 , K_3 , and an overall rate constant taken as floating parameters. The radius was taken as 14 Å.¹⁴ With the values of K , β , $[\text{X}]$, and $[\text{L}]$ given, the values for k_3 and k_4 were then adjusted to obtain a good fit to the data of Figure 2.
- (14) We simply added 1 Å for the methyl groups to the distance parameter of 13 Å used in the earlier study.²
- (15) The K_1/K_2 ratio of 1.47 would seem unexpectedly low. From recent conductance measurements on a similar system, viz. $\text{Fe}(\text{dmsO})_6(\text{ClO}_4)_3$ in dmsO solvent, an even lower ratio of 1.03 for the two association stages ($K_1 = 216 \text{ M}^{-1}$ and $K_2 = 210 \text{ M}^{-1}$) has been suggested (Pethybridge, A. D.; Puchalska, D. Presented at the 8th International Symposium on Solute-Solute-Solvent Interactions, Regensburg, FRG, Aug 9-14, 1987; poster 2.12).
- (16) The experimental evidence for this alternative is provided by a current investigation on the reductions of iron(III) trimethyl phosphate (tmp) complexes by methylferroins in MeCN.¹⁷ These reactions go to completion even in the presence of a high tmp level, allowing salt dependence studies to be made under various conditions. Whereas without adding extra tmp (FeL_3^{3+} is predominantly reacting) the rate shows a saturation dependence on salt similar to that in Figure 2, there is an almost linear increase when extra tmp (0.2 M) is present (FeL_4^{3+} is predominantly reacting).
- (17) Schmid, R.; Han, L. F.; Kirchner, K.; Sapunov, V. N. To be submitted for publication.

- (18) Borchardt, D.; Wherland, S. *Inorg. Chem.* **1984**, *23*, 2537.
- (19) Other cases concern first-order processes. (See, for example: Tachiyashiki, S.; Yamatera, H. *Inorg. Chem.* **1986**, *25*, 3209. Rotzinger, F. *Inorg. Chem.* **1988**, *27*, 768.)
- (20) Borchardt, D.; Wherland, S. *Inorg. Chem.* **1986**, *25*, 901.
- (21) Schmid, R.; Jedlicka, R. Research in progress.