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Redox Kinetics of Metal Complexes in Nonaqueous Solutions: Reductions of Tris(1,10-phenanthroline)- and Tris(2,2′-bipyridine)iron(III) by Hexakis(*N*,*N*-dimethylformamide)iron(II) in Acetonitrile: Role of First-Coordination Sphere

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The outer-sphere reduction of Fe(phen)$_3^{3+}$ by Fe(dmf)$_6^{2+}$ in acetonitrile (MeCN) with both salts added as the perchlorates exhibits a reaction order of 3 with respect to the reductant in the case of constant ionic strength (adjusted by Bu_4NClO_4) and even 4 when no electrolyte was added. The high order is due to fast solvation preequilibria between *N*,*N*-dimethylformamide (dmf) and MeCN coordinated at Fe^{2+}. Evidence involving speciation studies using IR and NMR spectroscopy is presented in favor of the bis(*N*,*N*-dimethylformamide) complex Fe(dmf)$_2$(MeCN)$_4^{2+}$ being the predominant species in the millimolar concentration range whereas the tetrakis(*N*,*N*-dimethylformamide) complex Fe(dmf)$_4$(MeCN)$_2^{2+}$ is the first one of the series to react ($k = 2\ (\pm 1) \times 10^7\ M^{-1}\ s^{-1}$, 25 °C, infinite ionic strength). When extra dmf is added, Fe(dmf)$_5$(MeCN)$^{2+}$ also reacts ($k = 4\ (\pm 3) \times 10^8\ M^{-1}\ s^{-1}$, again with no electrostatic interaction), and this reactivity increase is mainly a driving force effect on the basis of Marcus theory. The following solvation equilibrium constants (M^{-1}) have been obtained: Fe(dmf)$_2$(MeCN)$_4^{2+}$ + dmf = Fe(dmf)$_3$(MeCN)$_3^{2+}$ (0.3), Fe(dmf)$_3$(MeCN)$_3^{2+}$ + dmf = Fe(dmf)$_4$(MeCN)$_2^{2+}$ (30), and Fe(dmf)$_4$(MeCN)$_2^{2+}$ + dmf = Fe(dmf)$_5$(MeCN)$^{2+}$ (0.2). The further increase in reaction order when no electrolyte was added is very successfully accommodated by a rate law employing both ion pairing between Fe(phen)$_3^{3+}$ and ClO_4^- and ionic strength dependences through work terms for both the free-ion and the ion-paired paths. The ion-pairing tendency of some tetra-*n*-butylammonium salts with Fe(phen)$_3^{3+}$ increases in the order PF_6^- ($K_A = 1.4\ M^{-1}$) < BF_4^- (18) < ClO_4^- (71) < $CF_3SO_3^-$ (83). Finally, Fe(bpy)$_3^{3+}$ is less reactive than Fe(phen)$_3^{3+}$ by a factor of 1.14 although the redox potential difference of 67 mV would demand a factor of 3.7.

Introduction

The advantages of substitution-inert metal complexes in the study of the mechanisms of electron-transfer reactions are widely appreciated.[2-5] However, the problem of substitution-labile systems must be faced eventually because it is interesting by itself and because many practical redox agents are solvated metal ions. In the present paper we report the results of a kinetic investigation of very common redox couples, namely the reduction of tris(polypyridine)iron(III) complexes, Fe(phen)$_3^{3+}$ and Fe(bpy)$_3^{3+}$, by iron(II) in acetonitrile (MeCN). For the iron(II) reductant it has been found that Fe(OH$_2$)$_6^{2+}$ dissolved in MeCN does not reduce Fe(phen)$_3^{3+}$, whereas iron(II) added as the hexakis(*N*,*N*-dimethylformamide) complex Fe(dmf)$_6^{2+}$ does.[6] Since the latter forms relatively stable (and colorless) solutions in MeCN, it is a convenient reducing agent and has been reacted with the acetylacetonates of cobalt(III) and manganese(III),[7] and the oxinates of manganese(III)[8] and thallium(III).[9] These kinetic studies were motivated by the desire to learn about redox mechanisms in nonaqueous media but actually did not require one to search for solvate equilibria between dmf and MeCN (coordinated to Fe^{2+}). These equilibria, however, proved to be an essential feature of the profile of the title reactions. In fact, the analysis presented here appears to be a case study of solvate equilibria.

It should be mentioned that in 1976 we had made a preliminary study of these reactions.[6] Unfortunately, however, the earlier analysis proved to be erroneous.

Experimental Section

Materials. Fe(phen)$_3$(ClO$_4$)$_3$ was prepared in the usual manner and recrystallized four times from purified MeCN, giving a product that analyzed for the monohydrate, monoacetonitrile adduct, Fe(phen)$_3$(ClO$_4$)$_3$(H$_2$O)(MeCN).[10] In our former study[6] we used nitromethane–dichloromethane as recrystallization medium. By this procedure, however, as it turned out recently,[10] ferriin becomes contaminated by up to a few percent of Fe(phen)$_2$(CN)$_2$(ClO$_4$), which is considerably more reactive than ferriin. This is the reason for the occurrence of biphasic kinetics when Fe(dmf)$_6^{2+}$ reacts with ferriin present in large excess, which was formerly misinterpreted in terms of a slow equilibrium between differently active ferrous ion species. Fe(bpy)$_3$(ClO$_4$)$_3$ was prepared and treated analogously to ferriin. Fe(dmf)$_6$(ClO$_4$)$_2$[6] was made and MeCN and dmf were purified[10] as described. In the purification method for dmf, benzene/water was used as entrainer. For the kinetic measurements with extra added dmf we also used a sample of dmf distilled immediately before use over sulfuric acid and copper sulfate,[11] with identical results. Iron(II) perchlorate acetonitrile solvate was made according to Sisley et al.[12] As they also observed, analysis of the solid product indicated somewhat less than six acetonitriles per iron. Anal. Calcd for Fe(MeCN)$_6$(ClO$_4$)$_2$: C, 28.58; H, 3.57; N, 16.67; Cl, 14.07. Found: C, 26.16; H, 3.58; N, 15.18; Cl, 15.55. This analysis fits well to the monohydrate. The tetra-*n*-butylammonium salts of perchlorate,[13] tetrafluoroborate,[13] hexafluorophosphate,[14] and trifluoromethanesulfonate[15] were made and purified according to the references given.

Kinetics. The kinetic measurements were done at 25 °C on a Durrum D-110 stopped-flow spectrophotometer as before,[10] by following the formation of Fe(NN)$_3^{2+}$ (for phen, $\lambda_{max} = 508$ ($\epsilon = 11\,560\ M^{-1}\ cm^{-1}$); for bpy, $\lambda_{max} = 522$ ($\epsilon = 8850$)). When the reductant was taken in excess, the formation was perfectly first-order for at least 3 half-lives, and pseudo-first-order rate constants were obtained from the usual logarithmic plots of absorbance differences vs reaction times. All of the rate constants reported are average values from at least three parallel runs using different stock solutions and were reproducible to within ±5%. Further, from the total absorbance changes, quantitative conversion was ascertained. In contrast, reactions with Fe(NN)$_3^{3+}$ in excess were not quantitative and were too slow to warrant a detailed investigation. Thus the kinetic study to follow was based on the concentration dependences

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Table I. Dependence of the Pseudo-First-Order Rate Constant on the Concentration, $[Fe]_T$, of the Iron(II) Reductant Present in Excess[a]

$[Fe]_T$, mM	k_{obsd}, s^{-1}	k_{calcd},[b] s^{-1}	$[Fe]_T$, mM	k_{obsd}, s^{-1}	k_{calcd},[b] s^{-1}
0.5	0.0029	0.0032	5.0	23.4	25.1
1.0	0.0407	0.043	6.0	52.1	51.6
1.5	0.235	0.21	7.0	95.7	94.6
2.0	0.635	0.65	8.0	158	159
3.0	3.35	3.29	9.0	252	252
4.0	10.6	10.3			

[a] $[Fe(phen)_3^{3+}]$ = 0.1 mM: 25 °C; no electrolyte. [b] Calculated from eq 12 by using the parameters given in the first row of Table V and r = 13 Å.

of pseudo-first-order rate constants. Occasionally also the consumption of $Fe(NN)_3^{3+}$ (for phen; λ_{max} = 600 (ϵ = 830 M^{-1} cm^{-1}); for bpy, λ_{max} = 617 (ϵ 322)) was measured with results identical with those of $Fe(NN)_3^{2+}$ formation.

It should be mentioned that we also considered a mixing correction[16] for observed rate constants exceeding 100 s^{-1}, but any fit described in the following sections was actually deteriorated by any constants higher than the uncorrected ones. It may be that for MeCN solutions such corrections are not as important as for water for viscosity reasons.

Spectral Studies. The semiquantitative IR spectra of solutions of $Fe(dmf)_6(ClO_4)_2$ in MeCN were done in a 50-μm sodium chloride cell by using a Perkin-Elmer 225 grating spectrometer. The near-IR spectra shown in Figure 6 were recorded with a Cary 17D spectrophotometer. ^1H (270-MHz) NMR spectra of solutions of $Fe(dmf)_6(ClO_4)_2$ in CD_3CN (99.95% ^2D) were run on a JEOL GX-270 spectrometer with moisture ($[H_2O] \leq 10^{-4}$ M) and oxygen rigorously excluded.

Electrochemical Studies. Cyclic voltammetric (CV) measurements were carried out at 25 °C with a Princeton Applied Research (PAR) 173 potentiostat and a PAR 175 universal programmer equipped with a Houston Instruments Model 2000 XY recorder. A three-electrode system was used with a Pt or a glassy-carbon working electrode and a Pt-wire counter electrode. The reference electrode was $Ag/AgCF_3SO_3$ (10^{-2} M) in MeCN (Bu_4NClO_4/0.1 M)(against which bis(biphenyl)chromium (BCr) was oxidized at −1.027 V) for measuring $Fe(NN)_3^{2+/3+}$ and $Fe(MeCN)_6^{2+/3+}$ in MeCN. For solutions of dmf and dmf/MeCN mixtures, a silver wire was employed as a quasi-reference electrode (against which BCr was oxidized at −1.047 V). Both the counter electrode and the Ag-wire quasi-reference electrode were separated from the working solutions by fine-porosity glass frits. The reference redox system added to the solutions studied was bis(biphenyl)chromium(0)/bis(biphenyl)chromium(I) (BCr/BCr^+), added as the tetraphenylborate of the latter. $(TBA)PF_6$ (0.1 M) was used as supporting electrolyte. The voltammetric cell was made and the experiments were carried out as described by Gritzner.[17,18]

Tracer Experiments. A sample of $Fe(bpy)_3(ClO_4)_3$ prepared from iron wire enriched in iron-59 was dissolved in MeCN and reacted with $Fe(dmf)_6(ClO_4)_2$. The solution was then evaporated to dryness from where the iron(III) solvate was dissolved out by digesting with aqueous $NaClO_4$. The residue, containing the $Fe(bpy)_3(ClO_4)_2$, was dissolved in MeCN. Both solutions were assayed for iron-59 by a Ge(Li) detector connected to a γ-spectrometer showing that practically all of the iron-59 was in the $Fe(bpy)_3^{2+}$ moiety.

Results

Kinetic Studies. To begin with, the kinetics of reduction of both $Fe(phen)_3^{3+}$ and $Fe(bpy)_3^{3+}$ are in full conformity with each other, only with the rates of the former being slightly higher in value. Therefore, in the following, we shall delineate the phen system and just collect the corresponding constants for the bpy system in a footnote.

The pseudo-first-order rate constants were found to increase dramatically with excess of the reductant, resulting in an order of 4 for the condition of no added electrolyte and an order of 3 when the variation in ionic strength was compensated for by the addition of Bu_4NClO_4 (Figure 1, Table I). Further, Figure 2 shows the dependence of the rate constant on added Bu_4NClO_4 and other tetra-*n*-butylammonium salts as well. Finally, the rate constant was independent of deficient ferriin. Hence the reaction is first order in the latter.

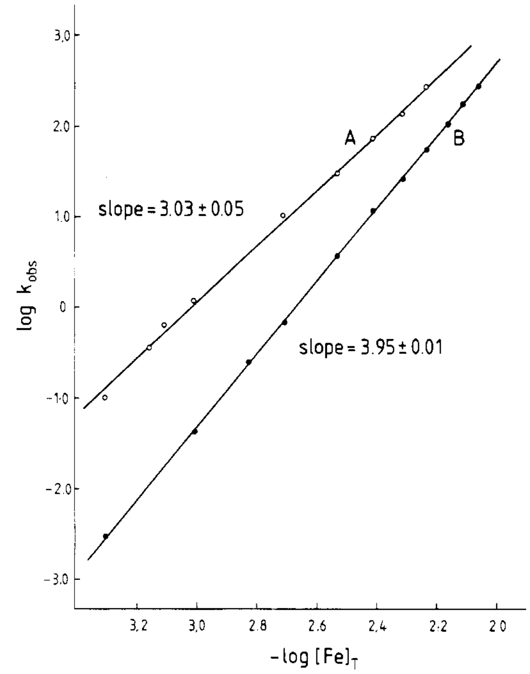

Figure 1. Order plots with respect to the total iron(II) concentration: (A) at constant ionic strength of 0.1 M; (B) without adding Bu_4NClO_4. $[Fe(phen)_3^{3+}]$ = 0.1 mM.

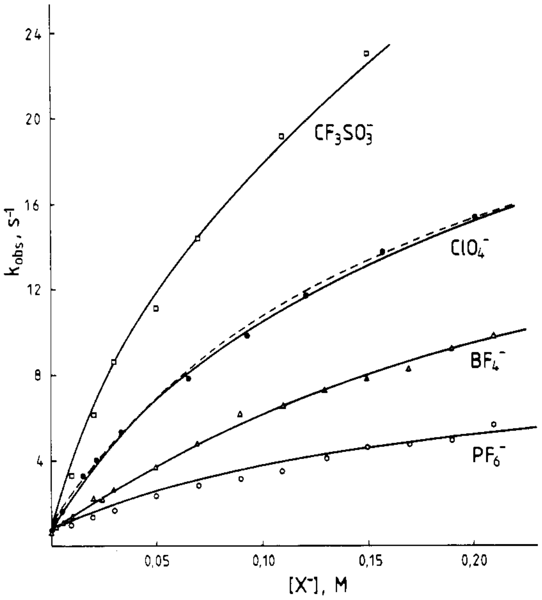

Figure 2. Dependence of the observed rate constant on added tetra-*n*-butylammonium salts ($[Fe(dmf)_6(ClO_4)_2$ = 2 mM; $[Fe(phen)_3(ClO_4)_3]$ = 0.1 mM). Solid lines are results of fits to eq 12 type equations. Table VI lists the fit parameters. The broken line was calculated from eq 12, assuming partial association of Bu_4NClO_4 and the fit parameters listed in the third row of Table V (see text).

The high reaction order in Fe(II) prompted us to study the effect of adding extra dmf. Essentially, there is a second-order dependence as is seen for the experimental series employing 1 mM Fe(II) concentration (Figure 3A). When dmf could be added in even larger excess (limited by the stopped-flow equipment) as was possible with 0.5 mM Fe(II), an effect toward saturation appeared (Figure 3B). In the other extreme, when the extra added dmf was not in large excess over that introduced by the reductant, the order plot was curved but became approximately linear with slope equal to 2 when 4 mol of dmf was allowed to be released from every mol of Fe(II) (Figure 4). The rate constants of two of the three series are given in Table II. At this juncture it is

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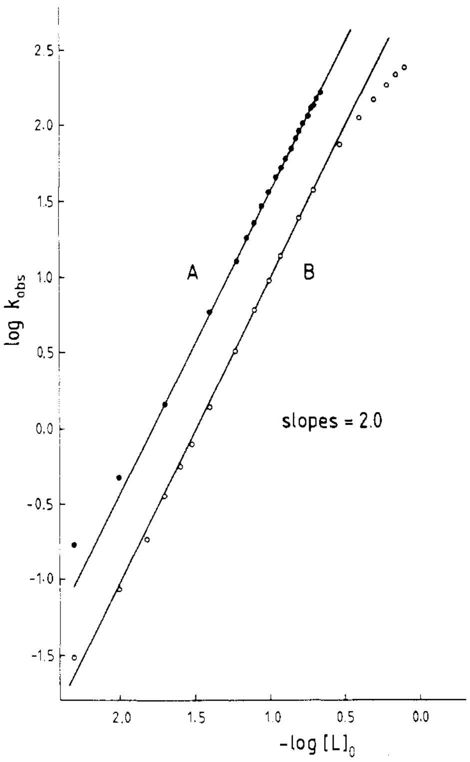

Figure 3. Order plots with respect to extra added dmf: $[Fe(dmf)_6(ClO_4)_2]$ = (A) 1 mM and (B) 0.5 mM; $[Fe(phen)_3(ClO_4)_3]$ = 0.1 mM.

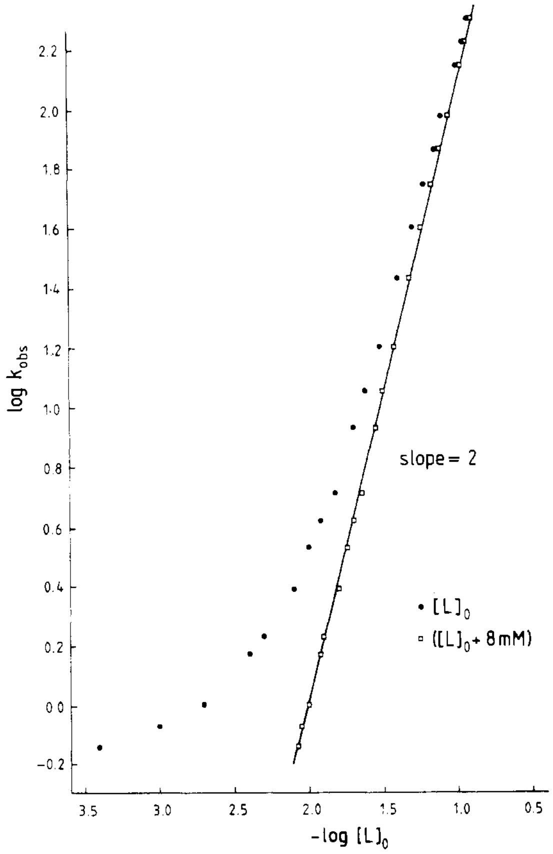

Figure 4. Order plot with respect to dmf for a reaction mixture of $[Fe(dmf)_6(ClO_4)_2]$ = 2 mM and $[Fe(phen)_3(ClO_4)_3]$ = 0.1 mM.

obvious that the elucidation of these redox reactions is not feasible without knowing the speciation of Fe(II). For this reason IR and NMR studies were performed.

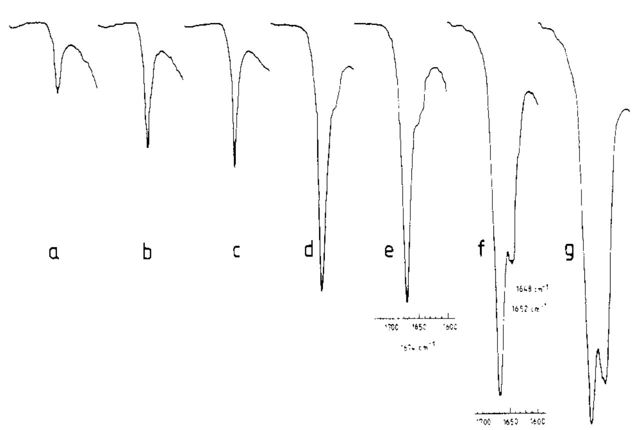

Figure 5. Parts of the IR spectra of solutions of $Fe(dmf)_6(ClO_4)_2$ in MeCN at room temperature: (a) 1 mM; (b) 2 mM; (c) 3 mM; (d) 8 mM; (e) 10 mM; (f) 20 mM; (g) 40 mM.

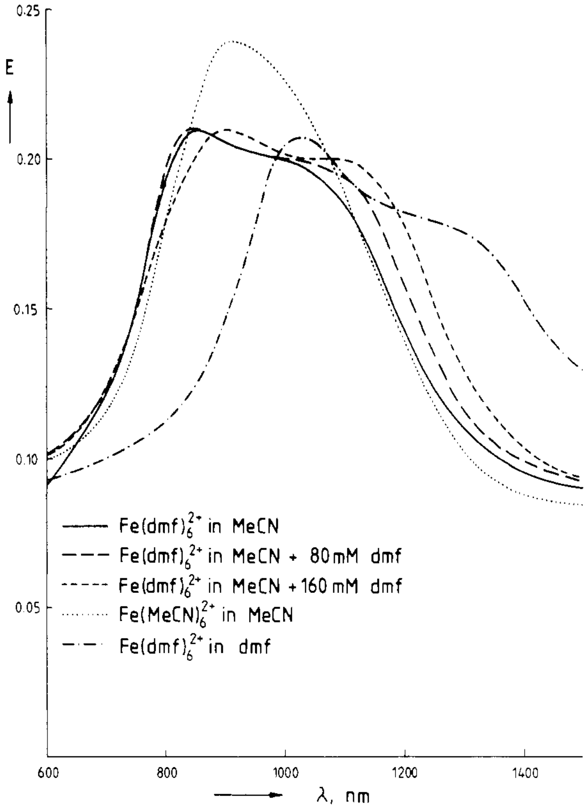

Figure 6. Near-IR spectra of iron(II) complexes recorded as ca. 2 mM solutions in 10-cm quartz cells at room temperature.

Speciation of Fe(II). IR Spectra. Up to 10 mM, solutions of $Fe(dmf)_6^{2+}$ in MeCN showed only displaced free dmf on the basis of the carbonyl stretching frequency at 1674 cm^{-1} (Figure 5) (lit.[19,20] 1675 cm^{-1}). From 10 mM upward, in addition, coordinated dmf became increasingly visible by a split band with peaks at 1652 and 1648 cm^{-1}. Such a frequency shift upon complexation is again in line with the literature.[19-21] The overlapping peaks of ligated dmf (the split band was treated as one) and free dmf were separated by fitting the experimental spectra with two Lorentzian curves. Evaluation of free dmf were then afforded by means of the extinction coefficient of 2.46 (±0.08) × 10^4 M^{-1} cm^{-1} of the free dmf carbonyl stretch as determined from a calibration curve. Finally, since the total amount of dmf was known, the intensity of the carbonyl stretch of complexed dmf would be indicated to be about 6.1 × 10^3 M^{-1} cm^{-1}. This is worth noting since usually the intensity of coordinated bands are found to be higher than that of free bands.[19] In the first row of Table

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Table II. Effect of Extra Added dmf, $[L]_0$, on the Pseudo-First-Order Rate Constant[a]

$[Fe]_T = 0.5$ mM				$[Fe]_T = 2$ mM			
$[L]_0$, mM	k_{obsd}, s^{-1}	k_{calcd},[b] s^{-1}	k_{calcd},[c] s^{-1}	$[L]_0$, mM	k_{obsd}, s^{-1}	k_{obsd},[b] s^{-1}	k_{calcd},[c] s^{-1}
0	0.0029	0.0028	0.0038	0	0.63	0.65	0.91
5	0.030	0.034	0.035	0.4	0.72	0.72	0.98
10	0.085	0.10	0.10	1	0.84	0.83	1.10
15	0.18	0.21	0.20	2	1.06	1.03	1.32
20	0.35	0.36	0.34	4	1.48	1.49	1.82
25	0.56	0.56	0.53	5	1.72	1.76	2.10
30	0.80	0.79	0.76	10	3.38	3.44	3.85
40	1.39	1.41	1.35	12	4.19	4.27	4.71
60	3.27	3.23	3.14	20	8.50	8.61	9.11
80	5.96	5.86	5.75	24	11.3	11.4	11.9
100	9.33	9.30	9.19	30	16.7	16.3	16.9
120	13.6	13.5	13.4	40	26.8	26.8	27.5
160	24.1	24.0	23.8	50	40.5	40.1	40.9
200	36.5	36.5	36.4	60	55.1	56.2	57.2
300	72.1	72.6	72.4	70	76.9	75.3	76.5
400	110	108	109	80	94.2	97.2	98.8
500	144	145	145	100	149	149	152
600	179	177	177	110	172	180	182
700	208	207	207	120	216	212	215
800	234	235	235				

[a] $[Fe(phen)_3^{3+}] = 0.1$ mM, no electrolyte, 25 °C. [b] Rate constant calculated from best-fit parameters to a rate law assuming that FeL_2^{2+} is predominant and both FeL_4^{2+} and FeL_5^{2+} react (see text). [c] Calculation similar to that of footnote *b*, assuming that FeL^{2+} is predominant and both FeL_3^{2+} and FeL_4^{2+} react (see text).

Table III. Numbers, $\bar{n}_{dmf}$, of Dimethylformamide Molecules Coordinated at Iron(II) in Solutions of $Fe(dmf)_6(ClO_4)_2$ in MeCN As Suggested from the Various Methods

$[Fe]_T$, mM	$\bar{n}_{dmf}$			
			kinetics	
	IR	NMR[a]	method 1[b]	method 2[c]
1	0.3		2.0	1.0
2	0.5		2.0	1.0
2.5		1.5 (±0.2)	2.0	1.0
3	0.2		2.0	1.0
8	1.2	1.8 (±0.3)	2.0	1.1
10	1.5		2.0	1.1
20	3.3		2.1	1.3
40	4.3		2.4	1.7
150		4.2 (±0.5)	3.3	2.6

[a] The NMR results though obtained at −42 °C may also be considered for room-temperature conditions as there is a negligible difference between the solvation enthalpies of Fe^{2+}–MeCN and Fe^{2+}–dmso (a donor similar to dmf) complexes (Libuš, W.; Mecik, M.; Strzelecki, *J. Solution Chem.* **1980**, *9*, 723). Actually, the IR intensities of the spectra shown in Figure 5 were not sensitive to temperature changes. [b] Calculated from the β values resulting from a fit of the dmf concentration dependences of the rate assuming that $Fe(dmf)_2(MeCN)_4^{2+}$ is predominant and both $Fe(dmf)_4(MeCN)_2^{2+}$ and $Fe(dmf)_5(MeCN)^{2+}$ react (see text). [c] Analogous to method 1 with the assumption that $Fe(dmf)(MeCN)_5^{2+}$ is predominant and both $Fe(dmf)_3(MeCN)_3^{2+}$ and $Fe(dmf)_4(MeCN)_2^{2+}$ react (see text).

III the results are presented in terms of the number, $\bar{n}$, of dmf molecules coordinated at Fe(II). That, however, some dmf remains coordinated even in the low-concentration range is shown by the near-IR spectra displayed in Figure 6. As to this, note the differences between the spectra of $Fe(MeCN)_6^{2+}$ and $Fe(dmf)_6^{2+}$ both dissolved in MeCN.

NMR Spectra. At temperatures of ca −42 to −46 °C (i.e., near solvent freezing) separate resonances of coordinated and bulk dmf could be detected in the ^1H NMR spectra of $Fe(dmf)_6(ClO_4)_2$ dissolved in CD_3CN. This is illustrated in the 8 mM solution spectrum in Figure 7 (upper curve). The mole fraction of coordinated dmf was calculated from the ratio of the area of the peaks between 10 and 30 ppm (assigned to methyl protons of coordinated dmf) and the area of the peak at 6 ppm (assigned to formyl protons of free dmf). The assumption that the 10–30 ppm signals do not include coordinated protons is reasonable from the experience that, in the case of dmf coordination via the oxygen, paramagnetic line broadening is about 10–50 times stronger for formyl protons than for methyl protons.[22,23] This view is further supported by the appearance of a broad band at 82 ppm (width of ca. 2200 Hz)(not shown in Figure 7). Though difficult to integrate, this signal can be said to represent the total formyl resonance within an error of ±20% to ±30%. Further, the assumption that the 6 ppm signal represents the total formyl resonance of free dmf was checked by comparing it with the signal near 0 ppm (free methyl protons), yielding a peak area ratio close to 1:6.

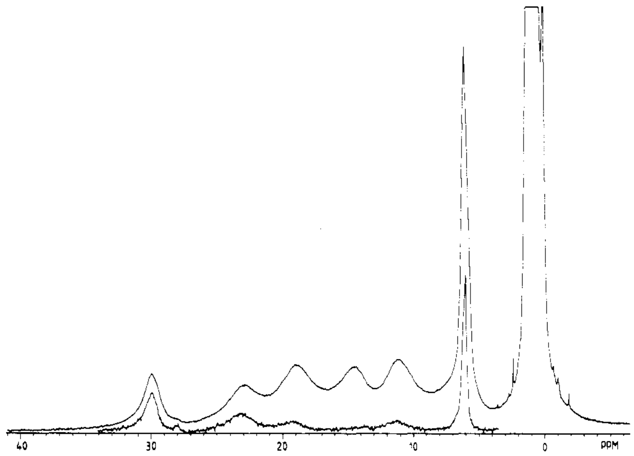

Figure 7. 270-MHz ^1H NMR spectra of $Fe(dmf)_6(ClO_4)_2$ in CD_3CN (99.95%) at −42 °C: upper curve, 8 mM; lower curve, 2.5 mM. The methyl signals of coordinated dmf were shifted to low field by 10–30 ppm. At 6 ppm the formyl signal is observed, and near 0 ppm the methyl signal of bulk dmf is observed. At 0 ppm, the rest protons of CD_3CN give a signal.

In addition to the 8 mM solution, 2.5 and 150 mM solutions were also measured, with an observed increase in peaks of overlapping coordinated and free signals as the concentration increases. Accordingly, the 2.5 mM spectrum (lower curve in Figure 7) could be treated as above with somewhat more accuracy. On the other hand, in the 150 mM solution spectrum, the free formyl resonance could not be detected separately and appears to be concealed by that of coordinated methyl protons. A rough

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Table IV. Redox Potentials[a] for $Fe^{3+/2+}$ in Acetonitrile at 25 °C

complex	$E_{1/2}$,[b] V	complex	$E_{1/2}$,[b] V
$Fe(dmf)_6^{3+/2+}$ [c]	$+1.06_8$ (100)	$Fe(phen)_3^{3+/2+}$	$+1.83_6$ (105)
$Fe(bpy)_3^{3+/2+}$	$+1.76_9$ (122)	$Fe(MeCN)_6^{3+/2+}$	$+2.54_4$[d] (365)

[a] The potentials are referenced to BCr (−1.118 V vs ferrocene/ferrocenium). [b] $E_{1/2}$ taken as $(E_p^{red} + E_p^{ox})/2$. Numbers in parentheses are peak separations in millivolts. Scan rate = 100 mV/s, 0.1 M Bu_4NPF_6 was present, and reactant concentrations were ca 1 mM. [c] Measured in dmf; cf ref 24. [d] Similar values can be derived from literature data: 2.56 V is obtained coulometrically[25] vs a $Ag/AgNO_3$ (in MeCN) reference and converted by using $E°(Fe(phen)_3^{3+/2+}) = 0.84$ V vs the same reference;[26] 2.45 V is derived from measurements at glassy carbon[27] vs SCE and converted by using values for SCE vs aqueous Ag/AgCl = 21.6 mV and $E°(Fe(phen)_3^{3+/2+})$ vs Ag/AgCl = 1.133 V.[28] Finally, a value of 2.45 V is also suggested from ref 29, giving $E_p^{ox} = +1.8$ V for $Fe(MeCN)_6^{2+}$ vs Ag/AgCl, assuming a peak potential separation of 100 mV. In contrast, a value for $E°(Fe(MeCN)_6^{3+/2+})$ of 1.6 V vs NHE[30] is much too low.

estimate, however, of dmf coordination was achieved by comparing the areas of the peaks appearing between 7 and 18 ppm (predominantly coordinated methyl protons) to that of the near-zero peak (free methyl protons). It may be mentioned that all the areas were obtained by manual integration. The coordination numbers for dmf thus obtained are given in the second row of Table III.

Electrochemical Data. Redox potentials for the iron complexes available are summarized in Table IV. At the Pt working electrode neither $Fe(MeCN)_6^{2+}$, $Fe(dmf)_6^{2+}$, nor $Fe(dmf)_6^{3+}$, each dissolved in MeCN, is redox active within the available solvent limit. The same is true for the glassy-carbon electrode except that $Fe(MeCN)_6^{2+}$ shows a reversible oscillographic wave indeed. When millimolar concentrations of dmf are added, however, ill-defined and poorly reproducible CVs are obtained. (A similar effect is observed by comparing the CVs shown in Figure 1 of ref 27.) When more dmf is added, a reversible oxidation developed (peak splitting of about 110 mV) which shifted to less positive potentials as more dmf was present: (starting with ca. 1 mM $Fe(MeCN)_6^{2+}$) $E_{1/2}$ (vs BCr) = +1.224 V (0.5 M dmf), +1.220 (1 M), +1.203 (2 M), and +1.186 V (4 M). These potentials are close to that of the $Fe(dmf)_6^{3+/2+}$ couple (Table IV).

Discussion

Since there is no displacement of chelate ligands during the redox process as shown by tracer experiments and the kinetic profile, both the catalysis by dmf and the high reaction order with respect to the reductant point to solvation equilibria between dmf and MeCN coordinated at Fe^{2+}, with those ions of higher dmf content being the more reactive:

$$Fe(MeCN)_6^{2+} + dmf \overset{\beta_1}{\rightleftharpoons} Fe(MeCN)_5(dmf)^{2+} + MeCN \quad (1)$$

$$Fe(MeCN)_6^{2+} + 2dmf \overset{\beta_2}{\rightleftharpoons} Fe(MeCN)_4(dmf)_2^{2+} + 2MeCN \quad (2)$$

etc. These solvate equilibria are to be considered as fast preequilibria.[31] In the most general case, in which all species are reacting with different rate constants k_0, k_1 ..., the observed rate constant

$$d[P]/dt = k_{obsd}[Fe(phen)_3^{3+}] \quad (3)$$

would be given by (in the following equations dmf is denoted as L)

$$k_{obsd} = k_0[Fe(MeCN)_6^{2+}]\left(1 + \frac{k_1\beta_1}{k_0}[L] + \frac{k_2\beta_2}{k_0}[L]^2 + ...\right) \quad (4)$$

In terms of the total ferrous concentration

$$\begin{aligned}[Fe]_T &= [Fe(MeCN)_6^{2+}] + [Fe(MeCN)_5L^{2+}] + [Fe(MeCN)_4L_2^{2+}] + ... \\ &= [Fe(MeCN)_6^{2+}](1 + \beta_1[L] + \beta_2[L]^2 + ...)\end{aligned} \quad (5)$$

eq 4 is rewritten as

$$k_{obsd} = \frac{k_0[Fe]_T(1 + (k_1\beta_1/k_0)[L] + (k_2\beta_2/k_0)[L]^2 + ...)}{1 + \beta_1[L] + \beta_2[L]^2 + ...} \quad (6)$$

The finding that the reaction orders in both $[Fe]_T$ and extra added dmf are essentially integers would mean that there is one ferrous species predominant in solution and another one predominantly reacting. Furthermore, the latter could well contain two molecules of dmf more than the former one, judged from the third-order and second-order dependences on $[Fe]_T$ and [dmf], respectively, found at constant ionic strength (Figures 1 and 3). From quantitative NMR measurements (which of course are more precise than IR data) coordination numbers for dmf between 1 and 2 are indicated. As will be shown, it is reasonable to adopt the bis complex $FeL_2(MeCN)_4^{2+}$ as the primary species in solution and, consequently, $FeL_4(MeCN)_2^{2+}$ as the reactive species. In this case eq 6 becomes

$$k_{obsd} = \frac{k_4\beta_4'[Fe]_T[L]^2}{1 + \beta_3'[L] + \beta_4'[L]^2} \quad (7)$$

where $\beta_3' = \beta_3/\beta_2$ and $\beta_4' = \beta_4/\beta_2$. Finally, by substitution of $4[Fe]_T$ for [L], the third-order dependence in $[Fe]_T$ would result if the denominator terms are small compared to unity

$$k_{obsd} = 16\beta_4'k_4[Fe]_T^3 \quad (8)$$

Let us now consider the additional increase in rate with increasing $[Fe]_T$ when the variation in ionic strength was not compensated for by electrolyte (Figure 1). Indeed, the rate law to be developed should likewise accommodate the increase in rate upon addition of Bu_4NClO_4 at fixed $[Fe]_T$ as displayed in Figure 2. Within current theories[5] an excellent and consistent fit to both concentration dependences was achieved by taking into account ion pairing between the +3 cation and the counterion and an ionic strength dependence through electrostatic work for both the free-ion path and ion-paired path (eq 9–11), with the solvation

$$Fe(phen)_3^{3+} + ClO_4^- \overset{K_A}{\rightleftharpoons} Fe(phen)_3(ClO_4)^{2+} \quad (9)$$

$$Fe(phen)_3^{3+} + FeL_4(MeCN)_2^{2+} \xrightarrow{k_{40}} products \quad (10)$$

$$Fe(phen)_3(ClO_4)^{2+} + FeL_4(MeCN)_2^{2+} \xrightarrow{k_{41}} products \quad (11)$$

equilibria assumed to be unaffected by ionic strength. The rate law for this mechanism is given by eq 12a, where A is derived

$$k_{obsd} = \frac{\beta_4'k_{40}(e^{6A}) + \beta_4'k_{41}(e^{4A})K_A[ClO_4^-]_T}{1 + K_A[ClO_4^-]_T}(16[Fe]_T^3) \quad (12a)$$

from the usual expression (eq 12b) for the work required to bring

$$A = \frac{7.12(I)^{1/2}}{1 + 0.48r(I)^{1/2}} - \frac{15}{r} \quad (12b)$$

the reactants together[4] and applied to MeCN ($\epsilon = 37.5$, $T = 298$ K, r in Å),[32] where the ionic strength I was calculated by assuming total dissociation of both the electrolyte and the ferrous complex. In the procedure, the radius parameter r was first set equal to a variety of values, treating $\beta_4'k_{40}$, $\beta_4'k_{41}$, and K_A as variables in

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(31) Relevant solvent exchanges atFe^{2+} are reported to be in the range 5×10^4 to 5×10^6 s^{-1} (See, for example: Merbach, A. E. *Pure Appl. Chem.* **1982**, *54*, 1479).

(32) It may be noted that eq 12b is fully equivalent to the more usual form, in our case, $A = -15/(r[1 + 0.48r(I)^{1/2}])$.

Table V. Best-Fit Parameters $\beta_4'k_{40}$ (M^{-3} s^{-1}), $\beta_4'k_{41}$ (M^{-3} s^{-1}), and K_A (M^{-1}) Obtained from the Concentration Dependences of the Observed Rate Constants on Reductant and Electrolyte Bu_4NClO_4

	$I \rightarrow \infty$[a]			$I \rightarrow 0$[b]		
	from $[Fe]_T$[c]	from $[ClO_4^-]_T$	from $[ClO_4^-]$[d]	from $[Fe]_T$[c]	from $[ClO_4^-]_T$	from $[ClO_4^-]$[d]
$\beta_4'k_{40}$	2.05 (±0.6) × 10^8	1.36 (±0.8) × 10^8	5.35 (±1.7) × 10^8	2.02 (±0.7) × 10^5	1.34 (±0.7) × 10^5	5.27 (±1.9) × 10^5
$\beta_4'k_{41}$	3.21 (±0.2) × 10^8	4.35 (±0.1) × 10^8	5.34 (±0.1) × 10^8	3.18 (±0.2) × 10^6	4.31 (±0.1) × 10^6	5.29 (±0.1) × 10^6
K_A	74.0 (±21)	70.6 (±9)	26.2 (±10)	74.0 (±23)	70.6 (±9)	26.2 (±12)

[a] From a fit to eq 12, taking r = 13 Å. [b] From a fit to eq 12, leaving out the second term of the right-hand side of eq 12b and taking r = 13 Å. [c] In the fit of the iron(II) concentration dependence, eq 12a was treated in terms of $k_{obsd}/[Fe]_T^3$ so as to give due weight to the low-concentration data. [d] Calculated by assuming partial association of Bu_4NClO_4 (K_A was taken as 10 M^{-1}), and activity coefficients from the Debye–Hückel equation (r was taken as 6 Å for Bu_4NClO_4), following the iteration method described for example by Nielson and Wherland.[4]

Table VI. Best-Fit Parameters Obtained from the Electrolyte Dependences[a]

electrolyte	$10^{-8}\beta_4'k_{40}$, M^{-3} s^{-1}	$10^{-8}\beta_4'k_{41}$, M^{-3} s^{-1}	K_A, M^{-1}
$Bu_4N(CF_3SO_3)$	1.32	7.52 (±0.1)	83.3 (±8)
$Bu_4N(ClO_4)$		4.35 (±0.1)	70.6 (±9)
$Bu_4N(BF_4)$		2.98 (±0.1)	18.0 (±3)
$Bu_4N(PF_6)$		1.00 (±0.2)	1.37 (±0.8)

[a] Rate equation similar to eq 12; $[Fe(dmf)_6(ClO_4)_2]$ = 2 mM; $[Fe(phen)_3(ClO_4)_3]$ = 0.1 mM; 25 °C. Electrolyte concentration ranges may be seen from Figure 2.

the optimization routine and looking for consistency in these parameters for both concentration dependences. This was found only for the narrow range of r between 12.5 and 13.5 Å, and these distances are close to the sum of radii for the two reacting ions.[33] Henceforth r was fixed at 13 Å in all subsequent calculations. The fit parameters are given in the first and second rows of Table V. The quality of the fits are very good, as judged by a comparison of k_{obsd} with calculated rate constants in Table I and the fit line with the experimental points in Figure 2. The data could be fitted equally well to rate law 12, by using different values of the parameters, with the second term of the right-hand side of eq 12b left out, that is, by utilizing the Debye–Hückel equation. The only difference is that the rate constants so adjusted refer, in the former case, to infinite ionic strength and, in the latter, to zero ionic strength. The figures in Table V thus emphasize the considerable work contributions to the rate constants under discussion, noting an increase by 3 orders of magnitude for the reaction between +3 and +2 ions (7 Å radii) and by 2 orders of magnitude for that between +2 and +2 ions in going from zero to infinite ionic strength.

The larger value of $\beta_4'k_{41}$ over that of $\beta_4'k_{40}$ calculated for the condition of $I \rightarrow \infty$, i.e., in the absence of electrostatic work, could indicate some sort of superexchange mechanism, the more so as even a decrease in electron-transfer reactivity with ion pairing might be expected.[5] Therefore, we studied the effect of adding different tetra-*n*-butylammonium salts displayed in Figure 2. Fits of the data to an equation similar to eq 12, with the same assumptions, were again very successful (fit lines in Figure 2).[34] The results are summarized in Table VI, noting that $\beta_4'k_{41}$ differs more from $\beta_4'k_{40}$ the higher the association constant between ferriin and the anions, that is the higher the ion pairing tendency. In recent papers,[4,5,35,36] the Wherland group treated the salt dependence in certain outer-sphere redox reactions run in MeCN in terms of ionic strengths calculated by assuming partial association of the electrolyte Bu_4NBF_4. We used this method and re-treated the perchlorate dependence on the basis of eq 12 but with the use of free perchlorate concentrations and ionic strengths calculated through an iteration procedure involving the extended Debye–Hückel equation for the evaluation of activity coefficients. This resulted in fit parameters shown in the third (and sixth) row of Table V. Although the fit to the experimental points (broken line in Figure 2) is not improved over that assuming total electrolyte dissociation, the new values of $\beta_4'k_{40}$ and $\beta_4'k_{41}$ do no longer differ. Minor additional ion pairing reactions could, however, conceal some reactivity differences to be expected between the free ferriin ion and its ion pair. It should further be mentioned that attempts to include an ionic strength dependent ion-pairing equilibrium constant in eq 12 on the basis of Debye-Hückel activity coefficients proved to be unsuccessful. Similar problems have been noted quite recently by Wherland.[5]

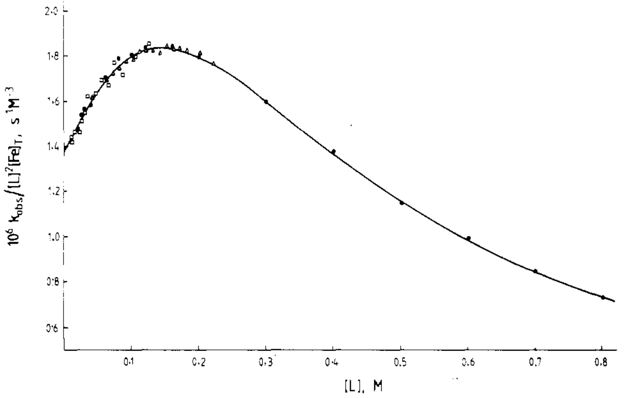

Figure 8. Dependence of the observed rate constant, $k_{obsd}/([L]^2[Fe]_T)$, on the free dmf concentration: $[Fe(dmf)_6(ClO_4)_2]$ = (●) 0.5 mM; (▲) 1 mM (0.546), and (□) 2 mM (0.278). In parentheses are given the mapping coefficients. $[Fe(phen)_3(ClO_4)_3]$ = 0.1 mM. The solid curve is a fit to eq 13 and 14 (see text and ref 38).

We now turn to discussion of the effect of extra added dmf, $[L]_0$. As may be shown by the data displayed in Table II, the expression $k_{obsd}/(([L]_0 + 4[Fe]_T)^2[Fe]_T)$, derived from eq 7, passes through a maximum in the course of increasing $[L]_0$. The increment at low $[L]_0$ requires a further solvate species namely $Fe(dmf)_5(MeCN)^{2+}$ to react. Therefore the variation in k_{obsd} with [L] was analyzed according to eq 13, where k_4 and k_5 are overall

$$\frac{k_{obsd}}{[Fe]_T[L]^2} = \frac{k_4\beta_4' + k_5\beta_5'[L]}{1 + \beta_3'[L] + \beta_4'[L]^2 + \beta_5'[L]^3} \qquad (13)$$

rate constants for the reactions of $Fe(dmf)_4(MeCN)_2^{2+}$ and $Fe(dmf)_5(MeCN)^{2+}$, respectively. The free dmf concentration was calculated from the roots of the material balance[37] through Newton's method, eq 14. Equations 13 and 14 were successively applied until, after three cycles, a consistent set of concentrations and β's was obtained. The results are shown graphically in Figure

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(33) The maximum distances from the Fe(II) center to the edge of dmf (see ref 41) and MeCN (see: Goedken, V. L.; Park, Y.; Peng, S. M.; Norris, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 7693) ligands (including the van der Waals radius of hydrogen) are estimated to be 7.5 and 6.1 Å, respectively. Thus for mixed complexes an average of 7 Å may be taken, which just equals that of the phenanthroline complex reactant (see ref 43 and further see: (a) Zalkin, A.; Templeton, D. H.; Ueki, T. *Inorg. Chem.* **1973**, *12*, 1641. (b) Baker, J.; Engelhardt, L. M.; Figgis, B. N.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1975**, 530).

(34) This is, to our knowledge, the first instance in which tolerably ensured estimates can be given for the ion-pairing equilibrium constants of a triply charged metal complex with some anions in a solvent of moderate dielectric constant. Recently, from preliminary conductance measurements with MeCN solutions of $Co(Me_2bpy)_3(ClO_4)_3$ a value of K_A = 10^3 has been proposed (Stalnaker, N. D.; Solenberger, J. C.; Wahl, A. C. *J. Phys. Chem.* **1977**, 81, 601).

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(37) Equation 14 was derived from eq 5 with the aid of a further material balance, $[L] - [L]_0 = 4[FeL_2^{2+}] + 3[FeL_3^{2+}] + 2[FeL_4^{2+}] + [FeL_5^{2+}]$.

$$[\mathrm{L}]^4 + [\mathrm{L}]^3\left(\frac{\beta_4'}{\beta_5'} - [\mathrm{L}]_0 - [\mathrm{Fe}]_\mathrm{T}\right) + [\mathrm{L}]^2\left(\frac{\beta_3'}{\beta_5'} - \frac{\beta_4'}{\beta_5'}[\mathrm{L}]_0 - \frac{2\beta_4'}{\beta_5'}[\mathrm{Fe}]_\mathrm{T}\right) + [\mathrm{L}]\left(\frac{1}{\beta_5'} - \frac{\beta_3'}{\beta_5'}[\mathrm{L}]_0 - \frac{3\beta_3'}{\beta_5'}[\mathrm{Fe}]_\mathrm{T}\right) - \left(\frac{[\mathrm{L}]_0}{\beta_5'} + \frac{4[\mathrm{Fe}]_\mathrm{T}}{\beta_5'}\right) = 0 \quad (14)$$

8. The constants so evaluated are $\beta_3' = 0.34$ (± 0.2), $\beta_4' = 10.48$ (± 0.4), and $\beta_5' = 2.24$ (± 0.7). The equilibrium constants (M^{-1}) are therefore

$$\mathrm{Fe(dmf)_2(MeCN)_4}^{2+} + \mathrm{dmf} = \mathrm{Fe(dmf)_3(MeCN)_3}^{2+} \qquad K = 0.3$$

$$\mathrm{Fe(dmf)_3(MeCN)_3}^{2+} + \mathrm{dmf} = \mathrm{Fe(dmf)_4(MeCN)_2}^{2+} \qquad K = 30$$

$$\mathrm{Fe(dmf)_4(MeCN)_2}^{2+} + \mathrm{dmf} = \mathrm{Fe(dmf)_5(MeCN)}^{2+} \qquad K = 0.2$$

This shows that the 2 to 4 and 4 to 2 complexes are particularly stable. Further, $\mathrm{Fe(dmf)_5(MeCN)}^{2+}$ is about 22 times more reactive than $\mathrm{Fe(dmf)_4(MeCN)_2}^{2+}$.[38]

The procedure was repeated with the assumptions that the $\mathrm{Fe(dmf)(MeCN)_5}^{2+}$ ion is predominant and that both $\mathrm{Fe(dmf)_3(MeCN)_3}^{2+}$ and $\mathrm{Fe(dmf)_4(MeCN)_2}^{2+}$ react, and the low $[\mathrm{L}]_0$ rate constants calculated from the best-fit parameters[39] are uniformly too high (see Table II). This is kinetic evidence in favor of the bis complex $\mathrm{Fe(dmf)_2(MeCN)_4}^{2+}$ being the primary species present in millimolar solutions of $\mathrm{Fe(dmf)_6}^{2+}$ in MeCN.

The following second-order rate constants ($M^{-1}\ s^{-1}$) (with no electrostatic interaction) can be given:

$$\mathrm{Fe(phen)_3}^{3+} + \mathrm{Fe(dmf)_4(MeCN)_2}^{2+} \rightarrow \text{products} \qquad k = 2(\pm 1) \times 10^7$$

$$\mathrm{Fe(phen)_3}^{3+} + \mathrm{Fe(dmf)_5(MeCN)}^{2+} \rightarrow \text{products} \qquad k = 4(\pm 3) \times 10^8$$

$\mathrm{Fe(bpy)_3}^{3+}$ is about 0.87 times as reactive[40] as $\mathrm{Fe(phen)_3}^{3+}$, and it is tempting, of course, to consider them from the point of view of the Marcus theory. This is used in the form (absence of electrostatic interactions, constants at 25 °C, the energetic terms in kcal mol^{-1}, the redox potential in V, and the quadratic term in ΔE omitted)

$$\ln k_\mathrm{calcd} = \ln A - 1.69[\Delta G_\mathrm{is}^* + \Delta G_\mathrm{os}^*] + 19.5\Delta E \quad (15)$$

where A is the preexponential factor, ΔG_is^* and ΔG_os^* are the inner-shell and outer-shell components of the intrinsic barrier, and ΔE is the difference in the redox potentials of the reactants. However, a full application of eq 15 requires so many assumptions that it becomes so uncertain that it is not useful. The analysis is hampered above all because the reduction potentials of the mixed Fe(II) complexes are not available except to note the 1.5 V difference between the values for $\mathrm{Fe(dmf)_6}^{2+}$ and $\mathrm{Fe(MeCN)_6}^{2+}$ (Table IV) thus suggesting a mean difference of 0.25 V for the replacement of one dmf by MeCN (although it is not to be expected that the reduction potential is simply a linear function of the number of dmf and MeCN ligands). Nevertheless it can qualitatively be shown that the rate variation is largely derived from changes in driving force as follows. Since the mean Fe(II)–O distance[41] of 2.12 Å and the Fe(II)–O stretching frequency[42] of 385 cm^{-1} in $\mathrm{Fe(dmf)_6(ClO_4)_2}$ are identical with the values reported for hexaaquoiron(II),[43,44] the reduced force constants for the Fe–O bonds may be assumed to be similar to that in the $\mathrm{Fe(OH_2)_6}^{2+/3+}$ couple (cf. ref 45), where in turn the value for the $\mathrm{Fe(OH_2)_6}^{3+}$ ion is taken to be similar to that of $\mathrm{Cr(OH_2)_6}^{3+}$.[44,46] Thus we take the reduced force constants in $\mathrm{Fe(dmf)_6}^{2+}$ and $\mathrm{Fe(dmf)_6}^{3+}$ to be 4.57×10^{28} and 7.88×10^{28} dyn cm^{-1}, respectively.[47] From these values and a difference in the iron–oxygen bond distances, Δd_0, of 0.14 Å,[44] ΔG_is^* is calculated[48] to be 0.34 kcal per mol of Fe–O(dmf) bond.[49] With this figure, the 22-fold reactivity of $\mathrm{Fe(dmf)_5(MeCN)}^{2+}$ over that of $\mathrm{Fe(dmf)_4(MeCN)_2}^{2+}$ would require a potential difference of 0.19 V from eq 15. This compares favorably with the mean difference of 0.25 V noted above.[50] Finally, the potential difference of 67 mV between $\mathrm{Fe(phen)_3}^{3+}$ and $\mathrm{Fe(bpy)_3}^{3+}$ would require the former to be 3.7 times more reactive compared to a factor of only 1.14 found experimentally.

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Registry No. $\mathrm{Fe(dmf)_6}^{2+}$, 62126-14-1; $\mathrm{Fe(phen)_3}^{3+}$, 13479-49-7; $\mathrm{Fe(bpy)_3}^{3+}$, 18661-69-3; $\mathrm{Fe(dmf)_2(MeCN)_4}^{2+}$, 113451-84-6; $\mathrm{Fe(dmf)_3(MeCN)_3}^{2+}$, 113451-85-7; $\mathrm{Fe(dmf)_4(MeCN)_2}^{2+}$, 113451-86-8.

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(38) In that iterative nonlinear least-squares treatment the three experimental series could be treated as one upon choosing the 0.5 mM Fe^{2+} curve as the standard and multiplying the $k_\mathrm{obsd}/([\mathrm{L}]^2[\mathrm{Fe}]_\mathrm{T})$ values for the 1 mM and 2 mM Fe^{2+} series by graphically determined mapping coefficients equal to 0.546 and 0.278, respectively. These are in close agreement with the ratios of no extra added dmf values of $k_\mathrm{obsd}/(16[\mathrm{Fe}]_\mathrm{T}^3)$ (Table I), indicating that k_5 and k_4 show the same variation with ionic strength and perchlorate concentration, and this is indeed reasonable. Thus 55 data points became available to elicit four parameters. For the 0.5 mM Fe^{2+} series, $k_4 = 1.32\ (\pm 0.05) \times 10^5\ M^{-1}\ s^{-1}$ and $k_5 = 2.97\ (\pm 0.6) \times 10^6$. (The products $k_4\beta_4'$ are also given from the Fe^{2+} concentration dependence.) It may be mentioned that, typically, $[\mathrm{L}]_0 \gg 4[\mathrm{Fe}]_\mathrm{T}$; therefore, little difference is brought about when taking $([\mathrm{L}]_0 + 4[\mathrm{Fe}]_\mathrm{T})$ instead of [L] in the plot displayed in Figure 8 (and this condition facilitated the assessment of trial values of the parameters).

(39) $\beta_2' = 1.38$, $\beta_3' = 12.50$, $\beta_4' = 5.41$, $k_3 = 9.5 \times 10^4$, and $k_4 = 1.90 \times 10^6$ (for the 0.5 mM Fe^{2+} series); notation is analogous to that used in the text.

(40) The experimental pseudo-first-order rate constants ($[\mathrm{Fe}]_\mathrm{T}$ (mM), $k_{\mathrm{obs}(}s^{-1}$)) for the reaction of $\mathrm{Fe(bpy)_3(ClO_4)_3}$ (0.1 mM) are as follows: 1, 0.0341 (0.0356); 2, 0.538 (0.577); 3, 2.74 (2.85); 4, 9.13 (9.10); 5, 22.5 (22.3); 6, 44.6 (46.2); 7, 85.3 (85.3); 8, 146 (144). In parentheses are given the rate constants calculated from eq 12 and the fit parameters $\beta_4'k_{40} = 1.31\ (\pm 0.6) \times 10^8\ M^{-3}\ s^{-1}$, $\beta_4'k_{41} = 3.10\ (\pm 0.3) \times 10^8$, and $K_\mathrm{A} = 71.3\ (\pm 15)\ M^{-1}$. Both the average factors of $k_\mathrm{obsd}(\mathrm{phen})/k_\mathrm{obsd}(\mathrm{bpy})$ and $k_\mathrm{calcd}(\mathrm{phen})/k_\mathrm{calcd}(\mathrm{bpy})$ are equal to about 1.14.

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(49) Compared to that, the changes in the Fe–N(MeCN) bond lengths might be minor on the basis of the π-bonding ability of MeCN.

(50) These considerations are qualitative only since with a thermodynamic driving force of 0.25 V, the quadratic term in eq 15 should not be ignored. It will change k_calcd by a factor of ~2.