Kinetics of Reduction of Hexakis(acetamide)- and Hexakis(dimethylacetamide)-iron(III) by Tris(3,4,5,6,7,8-hexamethyl-1,10-phenanthroline)iron(II) in Acetonitrile†

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The kinetics of outer-sphere electron transfer between $[Fe(hmphen)_3]^{2+}$ (hmphen = 3,4,5,6,7,8-hexamethyl-1,10-phenanthroline) and substitutionally labile Fe^{3+} introduced as $[FeL_6]^{3+}$ [L = dma (dimethylacetamide) or aa (acetamide)] in acetonitrile has been studied at 25 °C with the salts added as the perchlorates. Both reactions can be described by one mechanism implying that the acidic hydrogens of aa do not appreciably complicate the issue. To accommodate the variations in the redox rate constants, three rapid solvation pre-equilibria $[FeL_6]^{3+} \rightleftharpoons [FeL_3]^{3+} + 3L$ (co-ordinated MeCN is omitted) have to be invoked where, for driving-force reasons, only $[FeL_4]^{3+}$ and $[FeL_3]^{3+}$ are redox-active. Further, the acceleration with salt is well described by ion pairing and ion tripling of the trivalent ions with perchlorate, treated in terms of the reduction in Coulombic repulsion in forming the precursor complexes. For the solvate speciation, the overall reaction rates are controlled by both the reactivities of the reacting species and their availabilities. In the context of previous work, the differences between the two reactions are as follows: the redox rate constants of the aa species are larger than those of the corresponding dma species, which is primarily a driving-force effect with dma being the stronger Lewis base; on the other hand, the availabilities of the reacting species are higher in the case of dma, contrary to expectation. On the balance of the experimental evidence available, it does appear that the stabilities of the $[FeL_6]^{3+}$ solvate species are not a function of the donor strength of L but rather of its size tentatively expressed by the effective molecular hard-sphere diameter.

This is another of our 'particularly heroic attempts'[1] to analyse the kinetics of non-aqueous, outer-sphere electron transfer between transition-metal complexes in which one reactant is substitution labile, exchanging ligands with solvent molecules.[2-6] In these studies[3-6] we have been using trivalent Fe^{3+} (and Mn^{3+} as well) as the oxidants, complexed by strong oxygen donors L such as dimethylformamide (dmf). The reducing agents, and simultaneously the indicators of the progress of reaction, were ferroins [equation (1)], where X is a

$$[FeL_6]^{3+} + [Fe(Xphen)_3]^{2+} \xrightarrow{MeCN} \text{products} \qquad (1)$$

methyl group introduced so as to shift the potential for quantitative conversion. All salts were added as the perchlorates. The reactions were all run in one solvent *viz.* acetonitrile (MeCN), in order to minimise non-co-ordinating (outer-sphere) solvent effects and to focus on co-ordinating (inner-sphere) solvent effects.

At the outset, we, naively, did not expect appreciable competition from MeCN with L for co-ordination to a triply charged cation, in the framework of hard–soft considerations. One of our goals in measuring electron-transfer rates of simple solvate complexes has been to investigate to what extent they follow the order of empirical solvent-basicity parameters such as the donor number, and eventually to undertake comparisons with theoretical predictions through structural parameters. However, the kinetics of reactions (1) was found to be especially complex because of the occurrence of typically three solvation (fortunately fast) pre-equilibria (2)–(4) (in the following, co-ordinated MeCN is omitted). Consequently, these systems seem to be a poor choice for the determination of definite outer-sphere electron-transfer rate constants. Thus, we changed the emphasis of our experiments to more qualitative aspects highlighting the problems of studies in non-aqueous solvents. Nevertheless, the variations of the experimental rate constant with concentration actually are very sensitive probes of both the solvate and the ionic speciations because each speciation leads to large changes in reactivity. The individual solvate species react at highly different rates due to the different natures of MeCN, which is a π-acid stabilising the divalent state, and hard L which stabilises the trivalent state. Thus, rates are strongly decreased upon small additions of extra L. For the ionic speciation, the +3/+2 charge type of redox reactions causes a strong Coulombic repulsion to be overcome in forming the precursor complex. The work against repulsion is reduced by ion association with the counter ions, affecting a strong acceleration of the rate when extra salt is added.

$$[FeL_6]^{3+} \overset{\beta_1}{\rightleftharpoons} [FeL_5]^{3+} + L \qquad (2)$$

$$[FeL_6]^{3+} \overset{\beta_2}{\rightleftharpoons} [FeL_4]^{3+} + 2L \qquad (3)$$

$$[FeL_6]^{3+} \overset{\beta_3}{\rightleftharpoons} [FeL_3]^{3+} + 3L \qquad (4)$$

Our method of analysing the kinetic data is to study several dependencies of the pseudo-first-order rate constant on the concentrations of oxidant, extra added salt and extra added L and fit them simultaneously by a unique rate constant equation featuring solvation equilibrium constants, ion-pairing constants and rate constants as parameters. This procedure in connection with the above-mentioned sensitivity of the fits to the individual parameters would appear to afford an adequate analysis despite

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† *Non-SI units employed:* Å = 100 pm, dyn = 10^{-5} N.

the large amount of parametrisation. In fact, the values of β obtained from the kinetic fits alone yield mean co-ordination numbers nicely consistent with those derived from ^1H NMR spectroscopy revealing ligated and free L in CD_3CN.[3,4] Furthermore, the ion-pairing constants were satisfactorily complemented numerically by conductance measurements.[6]

In the present paper we compare the reduction kinetics of Fe^{3+} complexed by dimethylacetamide (dma) and acetamide (aa) again in MeCN as the solvent. The purpose is twofold. (*i*) The role of acidic hydrogens in non-aqueous outer-sphere electron transfer is elucidated further. In the case of the reduction kinetics of $[Mn\{OC(NH_2)_2\}_6]^{3+}$ and $[Mn(dmso)_6]^{3+}$ (dmso = dimethyl sulfoxide) it was found[6] that perchlorate association is similar for both despite the presence of acidic hydrogens in urea. The question arises whether this result is of more general validity. (*ii*) The work adds to the data on the corresponding systems $[Fe(dmf)_6]^{3+}$ and $[Fe(tmp)_6]^{3+}$ (tmp = trimethyl phosphate) reported previously.[3,4] Of the various parameters involved, the possibility of gathering values of β_1 for various L is an intriguing one. This addresses a long-standing question as to the relevance of the donor number of L to the stability of unmixed $[ML_6]^{n+}$ complexes when both leaving and non-leaving ligands are the same. In the simple picture of the donor–acceptor model it was argued that, since five co-ordinated solvent molecules contribute to the overall acceptor strength of the remaining $[ML_5]^{n+}$ moiety, but only one ligand leaves for exchange, the latter might more readily dissociate the higher is the donor number of L.[7] This proposal has been offered to explain the order of solvent-exchange rates for a few unmixed complexes of Ni^{2+} and Co^{2+}.[8] Apart from this, experimental evidence is still missing owing to the lack of appropriate reaction systems.

Experimental

Hexakis(dimethylacetamide)iron(III) perchlorate was prepared by dissolving iron(III) perchlorate hydrate (5 g) (Aldrich) in purified dimethylacetamide (30 cm^3), with the temperature kept below 30 °C. Anhydrous diethyl ether was added until the solution turned cloudy and a heavier layer was observed. Upon keeping the solution at -20 °C overnight a microcrystalline precipitate formed. It was collected on a glass frit and washed with cold anhydrous diethyl ether. The yellow crystals were dried *in vacuo* at ambient temperature ($\approx$90% yield). This procedure was repeated twice. The product seems to be slightly hygroscopic in the solid state (Found: C, 32.95; H, 6.30; Cl, 12.00; N, 9.40. Calc. for $C_{24}H_{54}Cl_3FeN_6O_{18}$: C, 32.85; H, 6.20; Cl, 12.25; N, 9.60%).

Hexakis(acetamide)iron(III) perchlorate was synthesised by adding an excess of acetamide (ten-fold excess) (Merck, reagent grade) to a solution of iron(III) perchlorate hydrate (5 g) (Aldrich) and acetic acid anhydride (1 : 6 v/v) in MeCN. The green product was precipitated with diethyl ether, filtered off and dried *in vacuo* (yield 92%). It was recrystallised twice from MeCN (Found: C, 20.55; H, 4.30; Cl, 15.10; N, 12.00. Calc. for $C_{12}H_{30}Cl_3FeN_6O_{18}$: C, 20.35; H, 4.25; Cl, 15.00; N, 11.85%).

The complex $[Fe(hmphen)_3][ClO_4]_2$ (hmphen = 3,4,5,6,7,8-hexamethyl-1,10-phenanthroline) was prepared as described.[3] The solvents acetonitrile and dimethylacetamide were purified and dried by standard methods.[9]

Tetrabutylammonium perchlorate was synthesised from tetrabutylammonium hydroxide (Riedel de Haen) and perchloric acid (Loba, p.a.) and recrystallised from 50% (v/v) anhydrous ethanol–diethyl ether.[9]

CAUTION: Owing to the hazardous nature of metal perchlorates containing organic ligands, the drying temperature was kept below 50 °C. Only small amounts were synthesised at a time and handled with extreme care.

The kinetic measurements were done on a Durrum D-110 stopped-flow spectrophotometer at 25 ± 0.1 °C (equipped with a MGW Lauda TUK 30 thermostat and a MGW Lauda R42/2D thermosensor) using a 2 mm cell by following the consumption of $[Fe(hmphen)_3]^{2+}$ (λ_{max} = 513 nm, ε = 16 000 dm^3 mol^{-1} cm^{-1}). Pseudo-first-order conditions were maintained by taking a 10–100 fold excess of $[Fe(dma)_6]^{3+}$ or $[Fe(aa)_6]^{3+}$ over the reductant concentration ($\approx 5 \times 10^{-5}$ mol dm^{-3}). Absorbance data were processed as before.[5]

Proton NMR measurements were carried out on a Bruker AC 250 instrument operating at 250.13 MHz. Temperature was controlled within ±1 °C by using a Eurotherm AC TBL temperature controller. Temperature readings were calibrated against the temperature dependence of the proton chemical shift of ethylene glycol.[10] Deuteriated acetonitrile (CD_3CN, 99.95%; Aldrich) was used as the solvent, which was dried over 3 Å molecular sieves and purged with N_2 in order to remove oxygen. The cyclic voltammetric experiments were done as before.[6] Conductance measurements were done with a WTW-LF535 microprocessor conductivity meter fitted with a WTW-LTA1 electrode.

Results

Speciation of Fe^{3+}.—As in previous work,[3,4,6] attempts have been made to assess the speciation by means of ^1H NMR spectroscopy. For $[Fe(dma)_6][ClO_4]_3$ dissolved in CD_3CN ($\approx$17 mmol dm^{-3}), resonances of co-ordinated dma (δ 70–30 and 10 to -5) and bulk dma (δ 3.17, 3.11 and 1.94), relative to the residual protons of the solvent (δ 1.93 *vs.* $SiMe_4$), were resolved at room temperature. Unfortunately the substantial peak overlap defies a definite analysis. Qualitatively, however, from a comparison with spectra recorded for the $[Fe(dmf)_6]^{3+}$ analogue where peak separation was feasible, it can be implied that the loss of dma and dmf from the respective compounds is similar but probably greater in the case of dma. For $[Fe(aa)_6][ClO_4]_3$, on the other hand, no free aa could be detected in the CD_3CN solution obviously because of a superimposition of the bulk methyl protons by the solvent signal. Actually acetamide dissolved in CD_3CN exhibits a sharp singlet at δ 1.84, very close to that of the residual protons of the solvent. Beyond that, the signals of the amide protons are not suitable for studying the speciation because of broadening due to quadrupole relaxation of the adjacent ^{14}N.

Kinetics.—Since both the oxidants considered behave quite similarly, they are described together, termed as Fe^{III}. Throughout the iron(III) oxidant was taken in at least ten-fold excess, giving pseudo-first-order rate constants, k_{obs}. In addition, quantitative conversions were ascertained from the absorbance changes.

Values of k_{obs} were measured under a variety of conditions. They were found to increase non-linearly with $[Fe^{III}]$ when no electrolyte was added and to pass through a maximum when the variation in perchlorate concentration was compensated for by the addition of NBu_4ClO_4 (Fig. 1). The variation in rate constant with NBu_4ClO_4 at fixed $[Fe^{III}]$ is shown in Fig. 2. Finally, the rate constants decrease notably when extra L was added (Fig. 3), independently of whether L was admixed to the Fe^{III} or the $[Fe(hmphen)_3]^{2+}$ reactant solutions before the reaction.

Electrochemical Data.—Redox potentials are available for the unmixed complexes only (Table 1). Thus, a strong shift of E° is expected upon the addition of L to a MeCN solution of $[Fe(MeCN)_6]^{3+}$. This is in fact found but a detailed study is not worthwile because of the occurrence of an electrochemical–chemical–electrochemical–chemical mechanism[11] with too many unknowns (different solvation equilibria at both Fe^{2+} and Fe^{3+}).

Conductance Data.—The molar conductivities (S cm^2 mol^{-1}) measured in MeCN at 25 °C for concentrations (mmol dm^{-3}) in parentheses are as follows: $[Fe(dma)_6][ClO_4]_3$, 402 (0.998),

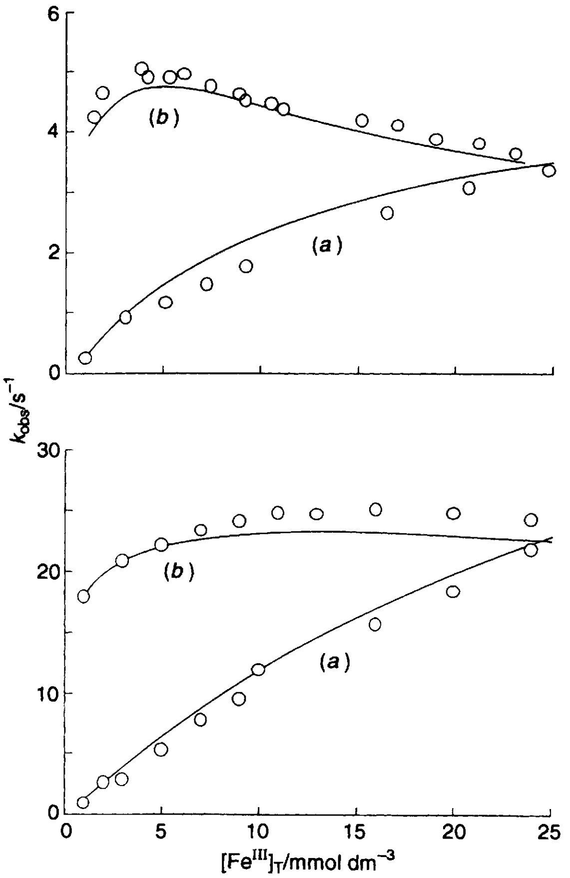


Fig. 1 Observed rate constant as a function of iron(III) concentration under different conditions. Curves: (*a*) without adding NBu_4ClO_4; (*b*) at constant total perchlorate concentration. L = dma (upper), $[Fe(hmphen)_3{}^{2+}]_T$ = 0.20 mmol dm^{-3}; aa (lower), $[Fe(hmphen)_3{}^{2+}]_T$ = 0.02 mmol dm^{-3}. Points are experimental, solid lines are calculated with equation (10) and parameters given in Table 2

Table 1 Redox potentials[a] in acetonitrile at 25 °C

Complex	$E_{\frac{1}{2}}{}^{b}$/V	Ref.
$[Fe(aa)_6]^{3+/2+}$	$1.22_0{}^{c}$	This work
$[Fe(dma)_6]^{3+/2+}$	$1.30_7{}^{d}$	This work
$[Fe(hmphen)_3]^{3+/2+}$	1.52_0	2
$[Fe(MeCN)_6]^{3+/2+}$	2.56_4	1

[a] The potentials are referenced to $[Cr(C_6H_5Ph)_2]^{0/+}$ (−1.118 *vs.* ferrocene–ferrocenium). [b] Potentials represent the mean of the cathodic and the anodic peak potentials from cyclic voltammograms (scan rate 0.1 V s^{-1}, electrolyte 0.1 mol dm^{-3} NBu_4ClO_4, reactant concentration ≈ 1 mmol dm^{-3}). [c] Measured in MeCN saturated with aa. [d] Measured in dma.

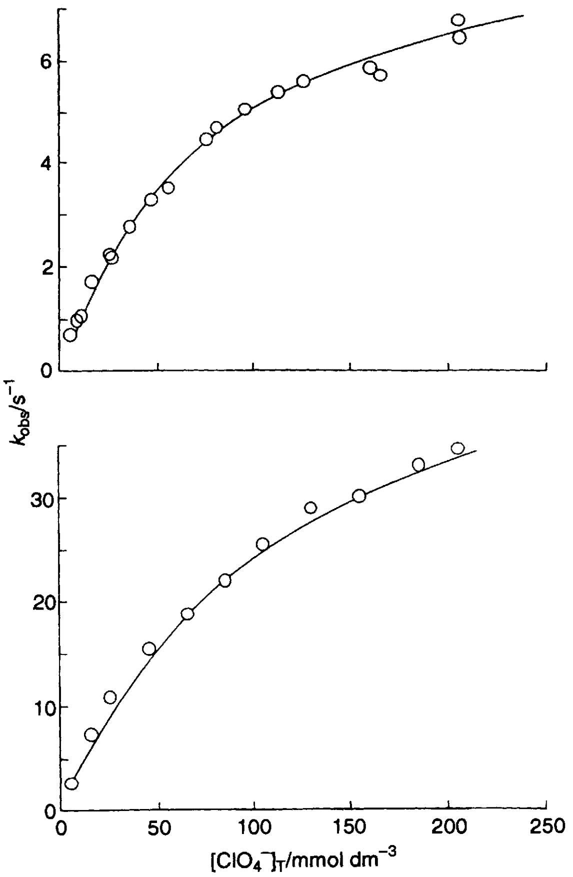


Fig. 2 Observed rate constants as a function of NBu_4ClO_4 salt concentration. Upper: $[Fe(dma)_6{}^{3+}]_T$ = 2.0 mmol dm^{-3}, $[Fe(hmphen)_3{}^{2+}]_T$ = 0.20 mmol dm^{-3}. Lower: $[Fe(aa)_6{}^{3+}]_T$ = 2.0 mmol dm^{-3}, $[Fe(hmphen)_3{}^{2+}]_T$ = 0.02 mmol dm^{-3}. Other details as in Fig. 1

367 (2.002), 345 (3.000), 331 (3.998), 319 (5.002), 309 (5.999), 302 (6.997), 294 (8.001), 287 (8.999) and 282 (9.997); $[Fe(aa)_6][ClO_4]_3$, 281 (3.999), 267 (5.002), 258 (6.000), 249 (7.002), 240 (7.998), 234 (9.001) and 229 (9.998). These results were analysed by the exact Lee–Wheaton equation[12] because no fit was obtained unless both higher terms were included. Various parameters were fixed before fitting: (*i*) the second-stage association constant $K_2{}^0$ was linked to the fitted value of $K_1{}^0$ by the Fuoss ratio [equation (5): D_s is the static dielectric constant and r the approach distance in Å]; (*ii*) the molar

$$K_1{}^0/K_2{}^0 = \exp(560.75/D_s r) \qquad (5)$$

conductance of perchlorate was taken as 103.8 S cm^2 mol^{-1};[13] (*iii*) the ratio of the conductance of the ion to that of the ion pairs $Fe(ClO_4)^{2+}\cdot Fe^{3+}$ and $Fe(ClO_4)_2{}^{+}\cdot Fe(ClO_4)^{2+}$ was set at 0.8 : 1 from past experience.

Owing to the high experimental concentrations chosen, values of both $K_1{}^0$ and $\lambda_0(\frac{1}{3}\,FeL_6{}^{3+})$, where λ_0 is the equivalent ionic conductivity, depend dramatically on r. Taking r = 9 Å, the Fuoss ratio, $K_1{}^0/K_2{}^0$, is equal to 5.27 and the results were, for $[Fe(dma)_6][ClO_4]_3$, $K_1{}^0$ = 740 dm^3 mol^{-1}, $\lambda_0[\frac{1}{3}Fe(dma)_6{}^{3+}]$ = 83.9 S cm^2 mol^{-1} and, for $[Fe(aa)_6][ClO_4]_3$, $K_1{}^0$ = 1410 dm^3 mol^{-1}, $\lambda_0[\frac{1}{3}Fe(aa)_6{}^{3+}]$ = 79.0 S cm^2 mol^{-1}. With r set at 10 Å (the Fuoss link is 4.46), the results were, for $[Fe(dma)_6][ClO_4]_3$, $K_1{}^0$ = 630 dm^3 mol^{-1}, $\lambda_0[\frac{1}{3}Fe(dma)_6{}^{3+}]$ = 78.9 S cm^2 mol^{-1} and, for $[Fe(aa)_6][ClO_4]_3$, $K_1{}^0$ = 1090 dm^3 mol^{-1}, $\lambda_0[\frac{1}{3}Fe(aa)_6{}^{3+}]$ = 69.9 S cm^2 mol^{-1}.

Discussion

In accordance with previous reports,[3–6] the decrease in rate when extra L is added, shown in Fig. 3, is indicative of solvation equilibria between L and MeCN co-ordinated at Fe^{3+}, with ions of higher L content being less reactive. The large effect of small additions of L would further suggest that not much ligand is lost from either complex. Moreover, since the effect of L is independent of the mode of addition (*i.e.*, either to the reductant or the oxidant solutions), these equilibria are rapid compared to the redox processes. The various solvate species available should have highly different reactivities. On the basis of Table 1, the reduction potential difference could well be about 0.2 V for the replacement of one L by MeCN.

In addition to the solvate speciation, also the ion speciation leads to large changes in reactivity. The problem of deconvoluting simultaneously these two kinds of speciation, is

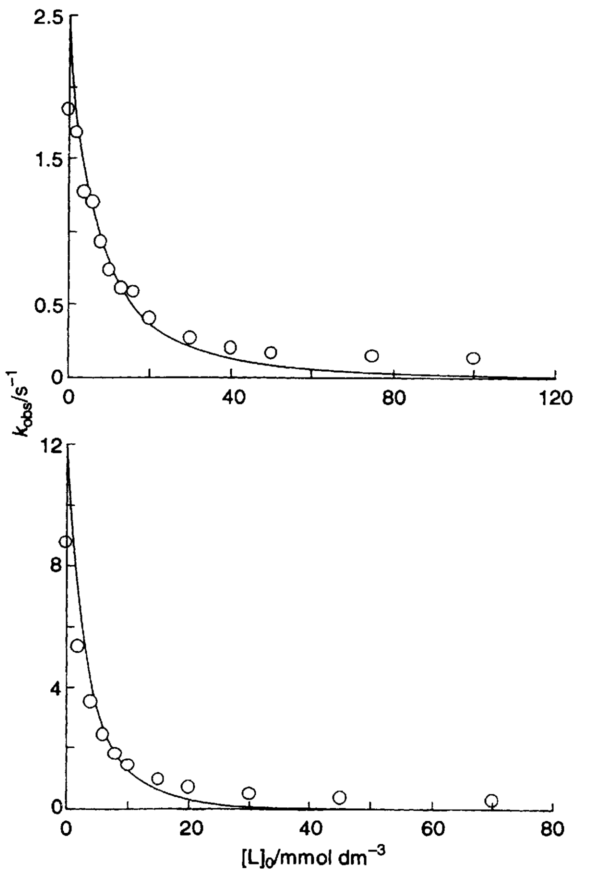


Fig. 3 Observed rate constants as a function of the concentration of extra added ligand. Upper: $[Fe(dma)_6{}^{3+}]_T$ = 10.0 mmol dm^{-3}, $[Fe(hmphen)_3{}^{2+}]_T$ = 0.20 mmol dm^{-3}. Lower: $[Fe(aa)_6{}^{3+}]_T$ = 10.0 mmol dm^{-3}, $[Fe(hmphen)_3{}^{2+}]_T$ = 0.025 mmol dm^{-3}. Other details as in Fig. 1

tackled by the reaction model successfully applied before[6] with all the assumptions made outlined as follows:

(*i*) The two kinds of speciation do not affect each other, that is ion association is qualitatively and quantitatively the same for all solvate species and *vice versa* (in the following, $X^- = ClO_4{}^-$), equations (6) and (7).

$$[FeL_n]^{3+} + X^- \underset{}{\overset{K_1}{\rightleftharpoons}} [FeL_nX]^{2+} \qquad (6)$$

$$[FeL_nX]^{2+} + X^- \underset{}{\overset{K_2}{\rightleftharpoons}} [FeL_nX_2]^{+} \qquad (7)$$

(*ii*) The reaction rate of each solvate species is considered to vary with both ionic strength and counter-ion concentration. Ionic strength effects are treated by Coulombic work terms with extrapolation to infinite ionic strength. Ion-pairing equilibrium constants are approximated as real constants within the experimental ionic strength range. Ion pairing lowers the electrostatic work needed to bring the reactants together by reducing the charge type of the reaction. Relative to this effect, ion pairing does not alter the electron-transfer reactivity. The ion-pairing constants calculated from the kinetic analyses should be connected with those derived from the conductance measurements *via* equation (8) valid for MeCN (D_s = 37.5,

$$K = K^0 \cdot \exp\frac{7.12 z_1 z_2 I^{\frac{1}{2}}}{1 + 0.48 r I^{\frac{1}{2}}} \qquad (8)$$

T = 298 K, z_1 and z_2 are the charges of the reactants, and r is the distance parameter in Å).[14] A justification of all these approximations has been given before.[5,6]

In addition to equations (6) and (7), slight ion pairing was also allowed for the ferroin reactant, equation (9), with K_3 fixed

$$[Fe(hmphen)_3]^{2+} + X^- \overset{K_3}{\rightleftharpoons} [Fe(hmphen)_3X]^+ \qquad (9)$$

at 3 dm^3 mol^{-1} as before.[3,4] Along these lines six ionic paths are considered for each solvate species, represented in turn by the six terms in the numerator of equation (10b) where the charge type enters *via* the exponential terms [*e.g.* the term e^{6A} stands for the free-ion path, *etc.* A is defined as in equation (10c)]. In this framework, the reactivity of each solvate species is characterised by a single electrostatics-free rate constant, independent of the number of anions attached.

For our two reactions the kinetics appear to be very similar as judged from the experimental rate constant plots in Figs. 1–3. One difference nevertheless is in the dependence of k_{obs} on $[Fe^{III}]_T$ of Fig. 1, measured at constant total perchlorate concentration. Whereas k_{obs} passes through a maximum in the case of dma, saturation behaviour is displayed in the case of aa. In terms of the various assumptions outlined above, the shape of these plots results from two combined effects: (*i*) the variation in the active species concentration with $[Fe^{III}]_T$, as determined by the solvation equilibrium constants, and (*ii*) the decrease in free $[ClO_4{}^-]$ due to ion association, as determined by the association constants. Since either ligand, dma and aa, is similar to dmf in both structure and donor strength, both reactions were analysed in terms of Scheme 1, by analogy to the Fe^{III}–dmf system.[3] (Here and in the following, the subscripts to the rate constants denote the number of L ligands bound.)

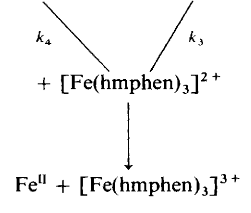
That $[FeL_4]^{3+}$ is the first species in the series to react in either case is reasonable in the context of the reduction potentials given in Table 1. If the potential is tentatively assumed to be a linear function of stoichiometry,[15,16] $[FeL_4]^{3+}$ is indeed the first species in the series that has a potential more positive than that of the ferroin oxidant. The expression for the pseudo-first-order rate constant with all assumptions described above included is given by equation (10a). The approach distance r was taken uniformly as 14 Å as

$$k_{obs} = Q\frac{k_3\beta_3 + k_4\beta_2[L]}{[L]^3 + \beta_1[L]^2 + \beta_2[L] + \beta_3}[Fe^{III}]_T \qquad (10)$$

$$Q = \frac{e^{6A} + K_1[X^-]e^{4A} + K_3[X^-]e^{3A} + K_1K_2[X^-]^2e^{2A}}{(1 + K_3[X^-])(1 + K_1[X^-] + K_1K_2[X^-]^2)} + \frac{K_1K_3[X^-]^2e^{2A} + K_1K_2K_3[X^-]^3e^{A}}{(1 + K_3[X^-])(1 + K_1[X^-] + K_1K_2[X^-]^2)} \qquad (10b)$$

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

before,[2,3] in the absence of structural data for the solvate complexes. It may be noted that the results of the calculations



Scheme 1 L = dma or aa

Table 2 Summary of association constants, solvation equilibrium constants and electrostatics-free rate constants for the oxidation of $[Fe(hmphen)_3]^{2+}$ in acetonitrile at 25 °C

	$[Fe(dma)_6]^{3+/2+}$	$[Fe(aa)_6]^{3+/2+}$
$K_1/dm^3\ mol^{-1}$	100 ± 20	180 ± 30
$K_2/dm^3\ mol^{-1}$	36.8 ± 6.3	11.6 ± 2
$\beta_1/mol\ dm^{-3}$	$(1.72 \pm 0.2) \times 10^{-2}$	$(6.56 \pm 0.6) \times 10^{-4}$
$\beta_2/mol^2\ dm^{-6}$	$(2.11 \pm 0.5) \times 10^{-5}$	$(1.37 \pm 0.4) \times 10^{-6}$
$\beta_3/mol^3\ dm^{-9}$	$(9.68 \pm 1.6) \times 10^{-8}$	$(1.41 \pm 1.3) \times 10^{-10}$
$k_4/dm^3\ mol^{-1}\ s^{-1}$	$(6.18 \pm 1.3) \times 10^3$	$(5.70 \pm 1.6) \times 10^4$
$k_3/dm^3\ mol^{-1}\ s^{-1}$	$(1.70 \pm 0.5) \times 10^4$	$(8.37 \pm 3.2) \times 10^5$

were not sensitive to moderate changes in the distance parameter. In fitting the kinetic data by use of equation (10), both the free proligand and the free perchlorate concentrations were supplied from the roots of the respective material-balance equations through Newton's method as before.[3]

The results of the fits are shown by the solid lines in Figs. 1–3, with the best-fit parameters listed in Table 2. Overall, the fits are quite acceptable apart perhaps from the rather poor reproduction of the saturation behaviour displayed by the aa system [lower plot (*b*) of Fig. 1]. As can be calculated from the β values of Table 2, for either ligand, both active species increase in concentration as $[Fe^{III}]_T$ increases {in contrast to the dmf case for which $[Fe(dmf)_3{}^{3+}]$ actually is found to decrease (see Fig. 5 in ref. 3)}. Thus the shapes of curves (*b*) in Fig. 1 are largely governed by the extent of ion association reducing $[ClO_4{}^-]_{free}$ as $[Fe^{III}]_T$ increases under the condition of constant $[ClO_4{}^-]_T$. Therefore, to obtain rate saturation instead of a maximum, the computer analysis based on equation (10) reduces K_2 for aa relative to that of dma, in contrast to expectation. What might be expected, however, is that K_2 be higher for aa similar to the K_1 values (Table 2), in accordance with the conductance data. For the latter, on the other hand, the Fuoss link [equation (5)] employed in treating them is likewise highly suspect. There is increasing evidence from various lines of inquiry, conductometric,[17,18] spectroscopic[19] and kinetic,[20–23] that the driving force in the ion-association process does not derive from the energy of the interaction between the cation and the anion, but instead from solvent–solute restructuring. Thus the occasional agreement between experimental association constants and those calculated from the Fuoss equation would seem to be rather fortuitous due to a compensation of various effects.

Anyway, the above comparisons may be taken to signal some additional complicating features inherent in the aa system, perhaps connected with the acidic hydrogens of aa, not accounted for by the reaction model employed here. Therefore, the physical significance of the numerical value of K_2 for the aa system cannot be taken too seriously. On the other hand, the differences in behaviour between the aa and dma systems, overall, are not so large so as to warrant a further analysis particularly since no simple modification of equation (10) is obvious. A prior comparison[6] between the reduction kinetics of $[Mn(dmso)_6]^{3+}$ and $[Mn\{OC(NH_2)_2\}_6]^{3+}$ did not reveal any particular effect of the acidic hydrogens of urea.

Let us now discuss the other parameters listed in Table 2. It should be emphasised that, because of the amount of parametrisation, the parameters themselves must have inherently rather large error limits. Particularly the error associated with the $[FeL_3]^{3+}$ path (β_3, k_3) is large. The mean co-ordination number of dma calculated from the β values for 8 mmol dm^{-3} of the dma salt is 5.05. For the aa salt of the same concentration the β values point to a significantly higher value of 5.62. In view of such high co-ordination numbers, clearly the fits of the kinetic data cannot be sensitive to β_3. An unexpected result is that the values of β are larger for $[Fe(aa)_6]^{3+}$ than for $[Fe(dma)_6]^{3+}$ despite the lower donor number of aa (26.0, see Appendix) compared to dma (27.8). In Fig. 4 are plotted values of β_1 (these are the most reliable ones, but similar plots are obtained using β_2 or β_3) *versus* the donor number including those for the complexes $[Fe(dmf)_6]^{3+}$ and $[Fe(tmp)_6]^{3+}$ dealt with before.[3,4] As is seen, there is definitely no relationship. Instead, there is a trend between β_1 and the ligand size tentatively expressed in terms of the effective hard-sphere diameter σ (see Appendix).[24–26] Although the ligand size is certainly not the only parameter determining the stability of complexes, this trend can be related to the size-dependent lability of the first co-ordination sphere to ligand substitution. Since local structural rearrangement is involved, such processes might better be described in terms of molecular packing effects rather than bond-strength parameters. Recently, there has been increasing appreciation of the fundamental importance of packing effects in liquid-state phenomena.[27–30] In a forthcoming study we will try to add to the number of data points in Fig. 4 by searching specifically for the effect of size by replacing the methyl groups in $[Fe(dmf)_6]^{3+}$ by higher homologues up to butyl.

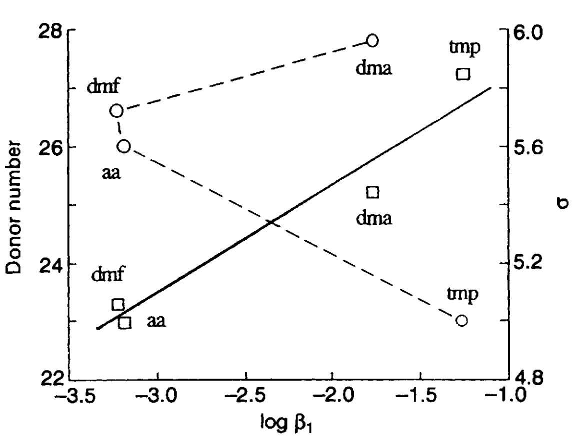


Fig. 4 Plot of log β_1 *vs.* donor number and σ of the ligands of $[FeL_6]^{3+}$

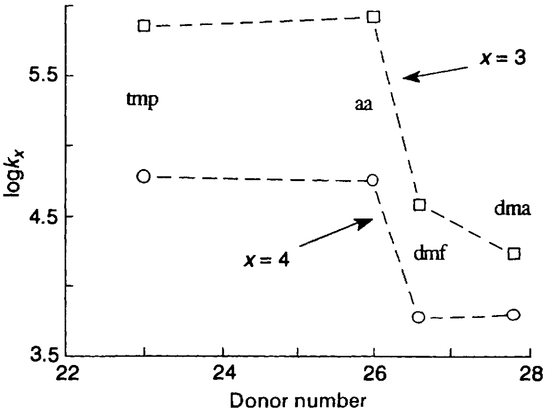


Fig. 5 Plot of log k_3 and log k_4 *vs.* donor number

For the (electrostatics-free) rate constants k_3 and k_4, finally, the complexes containing aa are more reactive towards reduction compared to the dma analogues. This may largely be a driving-force effect, aa being the weaker base thus stabilising the trivalent state to a lesser extent. However, the relationship between the rate constants and the ligand donor number is very poor as seen in Fig. 5.

An additional remark is in order here. In previous iron(III) systems[3,4] the experimental rate constants could not be fitted satisfactorily by equation (10) or a similar one unless the assumption was introduced that the various solvate species react *via* different ion-paired paths. This was rationalised[4] in terms of the competition of the driving force changing with the inner-sphere composition and of the Coulombic work changing with ion pairing. In fact, the change in driving force for the replacement of one L by MeCN could well be comparable in magnitude to the reduction in Coulombic work in changing the charge type from $+2/+3$ to $+2/+$, that is, when $[FeL_n]^{3+}$ reacts as such or as the triplet. Therefore, the overall reactivity of *e.g.* $[FeL_3]^{3+}$ might be comparable to that of $[FeL_4X_2]^+$. In the present iron(III) reactions, however, no improvement of the fits was attained upon this procedure.

Appendix

Determination of the Donor Number of aa.—This was done by a solvatochromic method reported recently.[31] Thus, the broad absorption peak at $\lambda \approx 602$ nm ($\tilde{\nu} \approx 16\,611$ cm^{-1}) displayed by [Cu(tmen)(acac)]ClO$_4$ (tmen = *N,N,N',N'*-tetramethylethane-1,2-diamine, acac = acetylacetonate) dissolved in nitromethane, saturated with aa, gives donor number = 26.0 from the empirical equation, $D_N = 195.5 - 0.0102\,\tilde{\nu}$, shown in the appendix of ref. 31.

Determination of the Hard-sphere Diameters σ.—(*a*) *Of aa.* This is done on the basis of the crystal structure of orthorhombic acetamide having dimensions $a = 7.76$, $b = 19.00$, $c = 9.51$ Å and $Z = 16$.[32] Hence the number density is $\rho = (abc/Z)^{-1} = 1.14 \times 10^{-2}$ Å^{-3}. From this, σ can be calculated from the equation $\eta = \pi\rho\sigma^3/6$ if the packing fraction η is known. Assuming closest packing, that is taking the maximum value of $\eta = \pi\sqrt{2}/6 = 0.74$, we obtain $\sigma = 4.99$ Å. Owing to the assumption of closest packing, this value should represent an upper estimate.

(*b*) *Of tmp.* For liquids, the hard-sphere diameter can be calculated by means of equation (29) of ref. 26, using experimental values of the isothermal compressibility β_T, the molar liquid volume, the gas-phase dipole moment, and the vapour pressure. However, β_T for trimethyl phosphate has not been measured. Thus we calculated β_T from the surface tension (36.92 dyn cm^{-1}) and the mass density ($d^{25} = 1.2144$ g cm^{-3}) according to ref. 33, giving $\beta_T = 6.88 \times 10^{-10}$ Pa^{-1}. From this we get $\sigma = 5.90$ Å. To check this, we used another empirical method, described in ref. 24, based on the molar refraction, requiring the refractive index $n = 1.3939$ and the number density $\rho = 5.204 \times 10^{-3}$ Å^{-3}. From these values the volume V_n can be evaluated from $[(n^2 - 1)/(n^2 + 2)]/\rho$ as 45.956 Å^3, and from the empirical correlation $V_{hs} = 2.473\,(V_n - 5.53)$ the hard-sphere volume $V_{hs} = 99.974$ Å^3. Finally, $V_{hs} = (\pi/6)\sigma^3$ giving $\sigma = 5.77$ Å. Thus we adopt for tmp, in Fig. 4, a value of $\sigma = 5.83$ Å as the mean.

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