Oxidation of 1,1′-Bis(methoxycarbonyl)ferrocene by Hexakis(*N,N*-dimethylformamide)iron(III) Perchlorate in Acetonitrile†

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The kinetics of the outer-sphere oxidation of 1,1′-bis(methoxycarbonyl)ferrocene, $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$, by substitutionally labile Fe^{3+} introduced as $[Fe(dmf)_6][ClO_4]_3$ (dmf = *N,N*-dimethylformamide) in MeCN as a solvent has been measured at 25 °C. The reactive species are $[Fe(dmf)_3(MeCN)_3]^{3+}$ and $[Fe(dmf)_4(MeCN)_2]^{3+}$ produced in fast pre-equilibria. This reaction system is compared to that of the oxidation of $[Fe(tmphen)_3]^{2+}$ (tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline) by the same oxidant reported previously. Since $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$ and $[Fe(tmphen)_3]^{2+}$ have nearly identical oxidation potentials, reactivity differences between them arise mainly from the different charge types of 0/3+ and 2+/3+. The rate constants for the reaction between $[Fe(tmphen)_3]^{2+}$ and Fe^{3+} extrapolated to infinite ionic strength are about three times greater than the corresponding values for the $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$–$Fe^{3+}$ reaction. This small difference is attributable to slightly higher bond distortional barriers towards oxidation of $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$ compared to $[Fe(tmphen)_3]^{2+}$. An interesting effect of adding tetrabutylammonium salts to the $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$–$Fe^{3+}$ reaction is observed. The anions BF_4^- and $CF_3SO_3^-$ slow down the reaction appreciably, whereas ClO_4^- and PF_6^- virtually do not affect the experimental rate constants.

The present study is a continuation of our ongoing kinetics work on electron-transfer reactions between metal complexes in non-aqueous solvents in which one reactant is substitutionally labile, exchanging ligands with solvent molecules. Although such systems are especially complex, they should continue to be studied as many practical redox agents are solvated metal ions. We are particularly interested in learning about the effect of ligated solvent molecules on redox reactivity in terms of empirical solvent basicity parameters such as the donor number (d.n.). Whereas relationships between redox potentials of solvated metal ions and d.n. are well-documented,[1] little is known about the variation in redox rates with ligated solvent molecules.[2,3]

In previous work we studied amongst others the oxidation of tris(3,4,7,8-tetramethyl-1,10-phenanthroline)iron(II), $[Fe(tmphen)_3]^{2+}$, by iron(III) introduced as $[Fe(dmf)_6]^{3+}$ (dmf = *N,N*-dimethylformamide) in acetonitrile (MeCN) with both salts added as the perchlorates.[3] This reaction was found to proceed as shown in equation (1) with solvate species

$$[Fe(dmf)_n(MeCN)_{6-n}]^{3+} + [Fe(tmphen)_3]^{2+} \longrightarrow \text{products} \quad (1)$$

concurrently existing for $n = 3$–6 among which, apparently for potential reasons (see Table 1), only the species with $n = 3$ or 4 are reactive. The various solvate species are highly different in reactivity since MeCN and dmf stabilise appreciably the divalent and trivalent states, respectively. The difference in the redox potentials between the couples $[Fe(dmf)_6]^{3+/2+}$ and $[Fe(MeCN)_6]^{3+/2+}$ is as high as 1.5 V.[3]

Table 1 Redox potentials[a] for $Fe^{3+/2+}$ in acetonitrile at 25 °C

Complex	$E_{\frac{1}{2}}{}^{b}$/V	Ref.
$[Fe(dmf)_6]^{3+/2+\,c}$	1.06_8	3
$[Fe(\eta\text{-}C_5H_5)_2]^{3+/2+}$	1.11_8	2
$[Fe(dmf)_5(MeCN)]^{3+/2+}$	1.32^d	
$[Fe(dmf)_4(MeCN)_2]^{3+/2+}$	1.57^d	
$[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]^{+/0}$	1.57_0	This work
$[Fe(tmphen)_3]^{3+/2+}$	1.57_5	3
$[Fe(dmf)_3(MeCN)_3]^{3+/2+}$	1.82^d	
$[Fe(MeCN)_6]^{3+/2+}$	2.56_4	2

[a] The potentials are referenced to $[Cr(C_6H_5C_6H_5)_2]^{0/+}$ (−1.118 V *vs.* ferrocene–ferrocenium). [b] $E_{\frac{1}{2}}$ taken as $(E_p{}^{red} + E_p{}^{ox})/2$. [c] Measured in dmf. [d] Interpolated on the tentative assumption that the reduction potential is a linear function of the dmf and MeCN ligands.

Besides solvate speciation the problem of ion speciation also has to be faced because of high reactant charges. The analysis of experimental rate constants in terms of definite ion-association constants and specific rate constants for free and ion-paired species is difficult and still remains an awkward problem due to the lack of particularly reliable theories. The procedure usually involves the introduction of a reference point given by either zero or infinite ionic strength.[4–6] Both reference points have their advantages and are dependent upon the system under investigation. In previous studies we used the latter approach and roughly approximated that the association constants are real constants in the experimental ionic strength range with the rate constants of the various ionic pathways extrapolated to infinite ionic strength.[2,3] Such 'electrostatics free' values can be compared directly with each other independently of reactant charges to assess the importance of any parameter other than charge, and this relatively simple model worked surprisingly well in describing all the experimental data.[2,3]

An opportunity to study the effect of charge on closely related redox systems arose when we tested ferrocene and some of its derivatives instead of iron–phenanthroline complexes as reducing agents. The compound $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$ was found to have nearly the same redox potential as $[Fe(tmphen)_3]^{2+}$ used in equation (1) (see Table 1). Moreover,

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† *Non-SI unit employed:* cal ≈ 4.184 J.

Table 2 Numbers, n_{dmf}, of *N,N'*-dimethylformamide molecules co-ordinated to Fe^{3+} in solutions of $[Fe(dmf)_6][ClO_4]_3$ in MeCN

$[Fe^{3+}]_T$/mmol dm^{-3}	NMR[a]	Kinetics[b]
1.70	5.19	4.99
3.03	5.32	5.25
6.86	5.55	5.53
8.60	5.72	5.59
9.24	5.75	5.61
21.2	5.77	5.77
76.5	5.90	5.90

[a] Uncertainty ±0.20. [b] Calculated from the β values as derived from the $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$ reaction (Table 3).

both reducing agents exhibit similarly small inner-shell barriers towards oxidation.[7–10] Thus, the difference in the redox kinetics to be found between these systems can largely be reduced to the effect of the different charge types 2+/3+ and 0/3+, although differences between the inner-shell and outer-shell barriers should be considered as well. The electrostatics-free rate constants obtained for equation (1) should be expected to approach the rate constant for the oxidation of $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$ where no Coulombic interactions are involved.

In the present study we report the kinetics of the oxidation of $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$ with $[Fe(dmf)_6]^{3+}$ in MeCN. Of additional interest is the effect of added electrolytes on the rate of the reaction. There are similar reactions for the 0/+1 and 0/+2 charge types that are sensitive to extra added salt,[11–15] while others are not.[16]

Experimental

The complex $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$ was purchased from Aldrich and purified by liquid chromatography with Al_2O_3 as the stationary phase and MeCN as the mobile phase; $[Fe(dmf)_6][ClO_4]_3$ was prepared by a standard method.[17]

CAUTION. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Therefore, the drying temperature was kept below 50 °C and the solid compounds handled with great caution.

Acetonitrile was purified as previously reported[2,18] while dmf was purified immediately before use by distillation over concentrated H_2SO_4 and anhydrous $CuSO_4$.[18] The tetrabutylammonium salts of ClO_4^-, BF_4^-, PF_6^- and $CF_3SO_3^-$ were made and purified as before.[2]

The kinetics were measured at 25 °C on a Durrum D-110 stopped-flow spectrometer as before[3] by following the formation of $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]^+$ (λ_{max} = 638 nm, ε = 460 dm^3 mol^{-1} cm^{-1}). Owing to the poor solubility of $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$ (≤1 mmol dm^{-3}), Fe^{3+} was used in excess in all experiments so as to obtain pseudo-first-order kinetics. The absorbance data were digitised by a D/A converter (Burr Brown Corp., System 20000) and transferred to a Commodore PC10 machine (Program 'Stopped-flow', Franz Apeltauer/TU-Vienna 1989/90). Pseudo-first-order rate constants were derived from non-weighted linear regression calculations using at least three half-lives. Data were fitted to the first-order equation, $\ln(A_\infty - A_t) = \ln A_0 - k_{obs}t$, where A_t, A_∞ and A_0 are the signals at time t, at the end, and at time zero of the reaction, respectively, and k_{obs} is the pseudo-first-order rate constant. The infinity readings were optimised and all rate constants reported are average values from at least five replicate experiments. With this procedure it was possible to determine the rate constants within ±5%.

The cyclic voltammetric measurements were carried out at 25 °C as before.[3] The ^1H NMR measurements were done on a Nicolet NT 200 WB instrument at 20 °C.[3] $[^2H_3]$Acetonitrile (MSD Isotopes Merck) was purified and stored as before.[3]

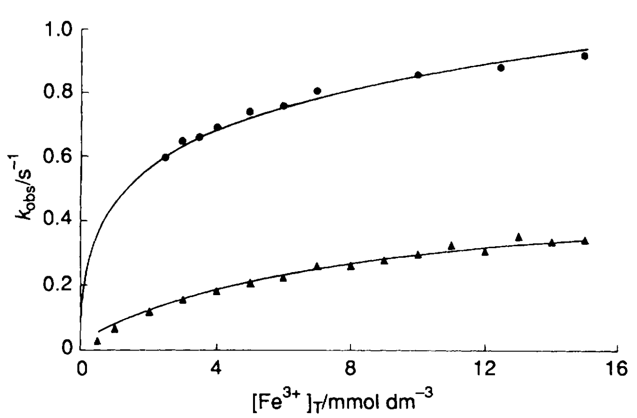


Fig. 1 Dependences of the observed rate constants for the oxidation of $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$ (0.5 mol dm^{-3}) (●) and $[Fe(tmphen)_3]^{2+}$ (0.1 mmol dm^{-3}) (▲) on the concentration of the Fe^{3+} oxidant in acetonitrile under the same conditions (25 °C, no extra added electrolyte)

Results

Speciation of Fe^{3+}.—In the ^1H NMR spectra of $[Fe(dmf)_6][ClO_4]_3$ dissolved in CD_3CN at 20 °C separate resonances for co-ordinated dmf and bulk dmf could be detected. Quantitative studies have already been described in the preceding paper.[3] However, in order to increase the precision of the following calculations speciation involving a few more concentrations have been determined. All co-ordination numbers thus determined are summarised in Table 2.

Kinetics.—The studies were performed under a variety of conditions. From a five-fold excess of Fe^{3+} upwards the reaction was practically pseudo-first order. The pseudo-first-order rate constant k_{obs} increased non-linearly with $[Fe^{3+}]$ in a saturating manner as shown in Fig. 1. The extent of reaction increased from 84% to a limiting value of 92%. The percentage conversions for the individual concentrations (millimolar amount of $[Fe^{3+}]$ in parentheses) were 84 (2.5), 87 (3.0), 88 (3.5), 88 (4.0), 90 (5.0), 90 (6.0), 91 (7.0), 91 (10.0), 91 (12.5) and 92 (15.0). The concentration of $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$ was 0.5 mmol dm^{-3}. According to Wherland and co-workers,[13,19] first-order analysis is adequate only when the reaction is more than 90% complete. Below that value an approach to equilibrium rate-law should be used, *e.g.*, pseudo-first order in the forward direction and second order with equal concentrations of the two reactants in the reverse direction. Such an analysis, however, needs the exact knowledge of the equilibrium constant which is not available in the present case (see Discussion). Therefore, at $[Fe^{3+}]$ < 5 mmol dm^{-3} values of k_{obs} as depicted in Fig. 1 are less accurate (±10%) but will certainly not alter the overall conclusions drawn from the plot.

When extra dmf was added the experimental rate constant decreased towards a limiting value with a simultaneous sigmoidal decrease in conversion. This is shown in Fig. 2. The results were independent of whether the dmf was admixed to the Fe^{3+} or the $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$ reactant solutions before the reaction. It is noteworthy that the decrease in conversion occurred at concentrations of extra added dmf lower than those in the $[Fe(tmphen)_3]^{2+}$–Fe^{3+} reaction despite the same driving force. The reason is concomitant decomposition of the $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]^+$ cation {which appears to be less stable than $[Fe(tmphen)_3]^{3+}$} in the presence of excess dmf caused by impurities of dmf or by dmf itself. This decomposition reaction was not investigated further but could well be similar to the reaction of unsubstituted ferrocenium in the presence of strong donor molecules reported elsewhere.[20]

Finally, the rate constants did not show a large variation upon the addition of NBu_4ClO_4 or NBu_4PF_6. In sharp contrast, $CF_3SO_3^-$ and BF_4^-, also added as the tetrabutylammonium salts, slowed down the reaction drastically as shown

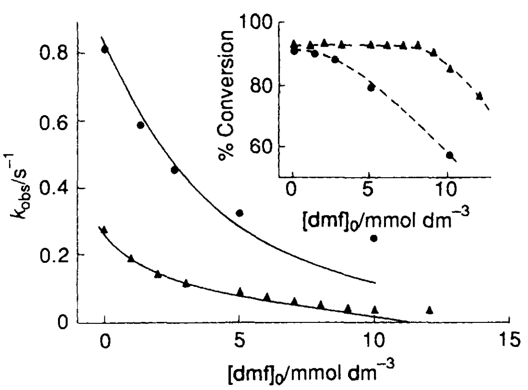


Fig. 2 Effect of extra added dmf on the observed rate constant and the degree of conversion (insert) for the oxidation of $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$ (0.5 mmol dm^{-3}) (●) and $[Fe(tmphen)_3]^{2+}$ (0.1 mmol dm^{-3}) (△) by Fe^{3+} (10 mmol dm^{-3}) in acetonitrile. Solid lines are calculated using the data given in Table 3, without consideration of the back reaction

Table 3 Comparison of solvation equlibrium constants and redox rate constants for the iron(III) oxidations of $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$ and $[Fe(tmphen)_3]^{2+}$ in acetonitrile

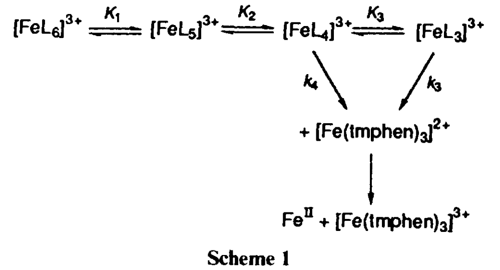
Parameter	$[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$	$[Fe(tmphen)_3]^{2+}$
β_1/mol dm^{-3}	2.9×10^{-4}	6×10^{-4}
β_2/mol^2 dm^{-6}	1.4×10^{-6}	5×10^{-7}
β_3/mol^3 dm^{-9}	1.0×10^{-10}	2×10^{-10}
k_4/dm^3 mol^{-1} s^{-1} [a,b]	6.0×10^2	2.4×10^2
k_3/dm^3 mol^{-1} s^{-1} [b,c]	6.2×10^3	1.9×10^4

[a] Reduction of $[Fe(dmf)_4(MeCN)_2]^{3+}$. [b] For the $[Fe(tmphen)_3]^{2+}$ reaction, electrostatics-free values are given. [c] Reduction of $[Fe(dmf)_3(MeCN)]^{3+}$.

in Fig. 3. These decreases in rates were accompanied by a decrease in conversion by *ca.* 10% upon the $CF_3SO_3^-$ and *ca.* 15% upon the BF_4^- additions whereas the degree of conversion was invariant with the two other salts.

Discussion

The decrease in rate when extra dmf was added (Fig. 2) indicates solvation equilibria between dmf and MeCN co-ordinated at Fe^{3+} with those ions of lower dmf content being the more reactive. Since the effect of dmf is independent of the mode of addition {*i.e.*, either to the $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$ or the Fe^{3+} solution} the solvation equilibria are fast compared to the redox process. These features have already been noted for the $[Fe(tmphen)_3]^{2+}$–Fe^{3+} system for which both the tris- and the tetrakis-dmf complexes were found to be the reactive species, Scheme 1 (dmf is denoted as L and co-ordinated MeCN is omitted).



Scheme 1

The quantitative evaluation of the solvation equilibrium constants from the kinetic data was complicated by the high reactant charges of +3/+2 bringing about strong ion association and ionic-strength effects. Therefore, two kinds of speciation, the ionic and solvate speciations, had to be considered simultaneously. Upon increasing the total Fe^{3+} concentration the non-linear increase in the experimental rate constant without any other salt added (lower curve in Fig. 1) is the result of three contributions: (*i*) the variation in the active species concentrations, (*ii*) increase in ionic strength and (*iii*) increase in the perchlorate counter ion concentration. In the data treatment the simplifying assumption was made that the two speciations are independent of each other, *i.e.*, ion association is qualitatively and quantitatively the same for all solvate species and *vice versa*. It is, further, assumed that the presence of anions does not significantly alter the electron-transfer reactivity of the precursor complexes. Co-ordination numbers of dmf obtained kinetically agree satisfactorily with those determined from ^1H NMR spectroscopic data.

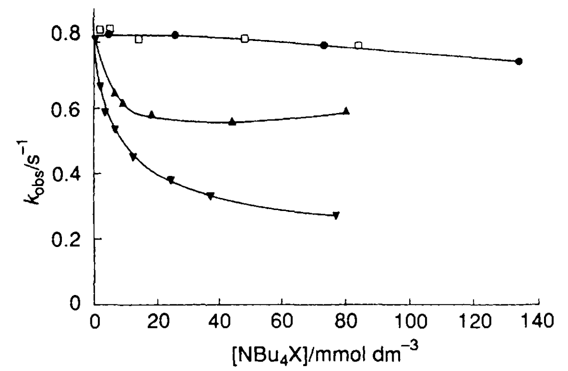


Fig. 3 Variation of the observed rate constant for the oxidation of $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$ (0.5 mmol dm^{-3}) by Fe^{3+} (10 mmol dm^{-3}) in acetonitrile with the addition of various tetrabutylammonium salts NBu_4X; X = PF_6 (□), ClO_4 (●), CF_3SO_3 (▲) or BF_4 (▼)

The present reaction between $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$ and Fe^{3+} formally eliminates the Coulombic interactions and in addition is not much affected by the presence of added perchlorate salt (Fig. 3). Therefore, the $[Fe^{3+}]_T$ dependence of the experimental rate constant (upper curve in Fig. 1) is predominantly associated with the variation of the active species concentration. In view of the same driving force for the $[Fe(tmphen)_3]^{2+}$ and $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$ reactions, it is reasonable to assume that the same solvate species are also reactive and equation (2) for the pseudo-first-order rate

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

constant should apply for the $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$ data where k_3 and k_4 are the second-order rate constants of reduction of $[FeL_3]^{3+}$ and $[FeL_4]^{3+}$, respectively, and $\beta_2 = K_1K_2$ and $\beta_3 = K_1K_2K_3$ (see Scheme 1). The experimental rate constants in Fig. 1, additionally including the data points for the three lowest $[dmf]_0$ values of Fig. 2, gave a good fit to equation (2) as seen by the full lines in the figures. In that procedure the free dmf concentration was obtained from the solution of the material balance equations through Newton's method as in ref. 3. Starting with the set of β values as calculated for the $[Fe(tmphen)_3]^{2+}$–Fe^{3+} system a non-linear least-squares regression yielded $\beta_1 = (2.9 \pm 0.3) \times 10^{-4}$ mol dm^{-3}, $\beta_2 = (1.4 \pm 0.1) \times 10^{-6}$ mol^2 dm^{-6}, $\beta_3 = (1 \pm 3) \times 10^{-10}$ mol^3 dm^{-9}, $k_3 = 6200 \pm 5000$ dm^3 mol^{-1} s^{-1} and $k_4 = 600 \pm 40$ dm^3 mol^{-1} s^{-1}. Errors were calculated from the method of supporting planes.[11] The considerable uncertainty in the values determined for the $[FeL_3]^{3+}$ path (k_3, β_3) is noted. To better quantitate this pathway we made use of the NMR data of Table 2 as follows. With the values for β_1 and β_2 fixed as obtained above, we varied β_3 so as to receive the closest reproduction of the NMR data. This procedure showed that $(1 \pm 0.5) \times 10^{-10}$ mol^3 dm^{-9} is the most reasonable value for β_3. Now introducing

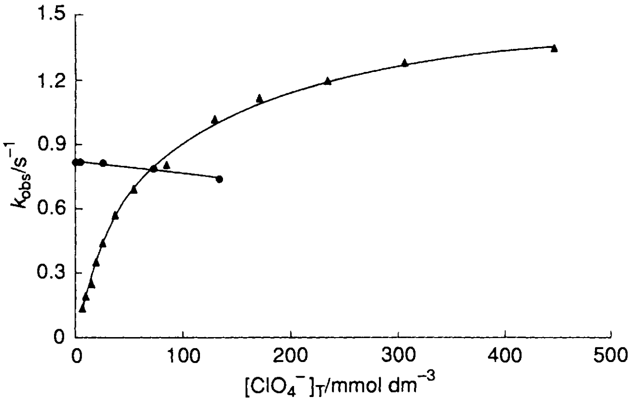


Fig. 4 Dependence of the observed rate constant for the oxidation of $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$ (0.5 mmol dm^{-3}) (●) and $[Fe(tmphen)_3]^{2+}$ 0.1 mmol dm^{-3}) (▲) by Fe^{3+} {$[Fe^{3+}]$ = 10 and 2 mmol dm^{-3} respectively} in acetonitrile on the addition of NBu_4ClO_4. The solid line for the latter reaction is calculated (ref. 3)

this value in equation (2) as a constant we obtained $k_3 = (6.2 \pm 1) \times 10^3$ dm^3 mol^{-1} s^{-1}. The β values determined in this manner are in good agreement with those derived from the $[Fe(tmphen)_3]^{2+}$ oxidation (see Table 2) and we therefore conclude that the approach to ionic speciation used before renders an adequate description of this complex reaction system.

The unexpectedly small differences in the experimental rate constants of the two systems under consideration displayed in Fig. 1, obtained under the same conditions {*e.g.*, at 10 mmol dm^{-3} Fe^{3+}, the $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$ reaction is only 2.8 times faster than the $[Fe(tmphen)_3]^{2+}$ reaction}, prompts comment. If the reactivity difference between both systems was entirely due to the difference in charge type, all other parameters being equal, the Coulombic work expression [see equations (3a) and (3b)][4] would predict (ion pairing neglected) a *ca.*

$$k = k_0\exp(-w/RT) \qquad (3a)$$

$$w = \frac{Z_1Z_2e^2N_A}{D_sr(1 + \beta r I^{\frac{1}{2}})} \qquad (3b)$$

15-fold retardation of a +2/+3 charge-type reaction relative to a reaction without any electrostatic work involved. One possibility to account for these discrepancies is to invoke ion pairing reducing the reactant overall charges. However, only when quantitative ion tripling between the Fe^{3+} species and ClO_4 is assumed, *i.e.* for +1/+1 charge-type, equation (3) would yield a value similar to the experimental reactivity difference. Thus, besides ion association, there must be an additional parameter for which the two systems differ. This is also anticipated from the salt dependence shown in Fig. 4 since in the presence of perchlorate electrolyte the $[Fe(tmphen)_3]^{2+}$ Fe^{3+} reaction becomes even faster than the $[Fe(\eta^5$ $C_5H_4CO_2Me)_2]$ analogue instead of approaching it as one would expect if the systems did differ only in the electrostatic work needed for precursor complex formation. An additional decrease in reactivity of the $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$ reaction relative to that of $[Fe(tmphen)_3]^{2+}$ is probably associated with a slightly higher bond distortional barrier for the former. From bond-distance and Raman spectroscopic data of ferrocenium and ferrocene, $\Delta G_{is}{}^*$ is estimated to be roughly 0.8 kcal mol^{-1}.[7,8] The value for the iron phenanthrolines is usually regarded as negligible.[9,10] A 0.8 kcal difference in $\Delta G_{is}{}^*$ would result in a reactivity difference of 3.8 on the basis of the Marcus theory equation used in the form given in ref. 2 [equation (4), absence

$$\ln k_{calc} = \ln A - 1.69[\Delta G_{is}{}^* + \Delta G_{os}{}^*] + 19.5\Delta E \qquad (4)$$

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, $\Delta G_{os}{}^*$ assumed to be equal for both systems] where A is the prefactor, $\Delta G_{is}{}^*$ and $\Delta G_{os}{}^*$ are the inner- and outer-shell components of the intrinsic barrier, and ΔE is the difference in the redox potentials of the reactants. A second contribution stems from the outer-sphere reorganisation energy, $\Delta G_{os}{}^*$, due to the different molecular size and shape of $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$ and $[Fe(tmphen)_3]^{2+}$, respectively. It is, however, difficult to account for these effects due to the lack of appropriate data, *e.g.* crystal structures. Qualitatively, however, owing to the expected smaller size of $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$ on the basis of Marcus theory a somewhat larger $\Delta G_{os}{}^*$ and thus a smaller rate constant should be anticipated and could also account for the reactivity difference between $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$ and $[Fe(tmphen)_3]^{2+}$.

The resulting 11-fold higher relative reactivity of $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$ with respect to $[Fe(tmphen)_3]^{2+}$ is still substantially lower than anticipated from equation (4). This discrepancy eventually is reconciled in terms of ion association. The latter effect is also apparent in Fig. 1 noting the small variation in the reactivity ratio with ionic strength from a value of 3.6 at 5 mmol dm^{-3} decreasing to 2.6 at 15 mmol dm^{-3} Fe^{3+}. This is a relative decrease by a factor of 1.4 compared to 2.5 predicted from equation (4).

Of further interest is the electrolyte dependence of this reaction shown in Fig. 3. Although there is no Coulombic repulsion between the reactants in forming the precursor complex, such reactions have often been found to still be affected by extra added salt. This is attributed to the formation of ion pairs which have lower reactivity than the free ions in the case of inadequate donor–acceptor orbital overlap further disturbed by the presence of an anion. On the other hand, the absence of a salt effect, although ion pairs are formed, is believed to signal good overlap irrespective of an anion present.[16]

In the present case, there is strong association between Fe^{3+} and ClO_4^- even to the extent of strong ion tripling.[3] The finding, then, that the $[Fe(\eta^5\text{-}C_5H_4CO_2Me)_2]$–$Fe^{3+}$ reaction is only slightly affected by either NBu_4ClO_4 or NBu_4PF_6 would classify this system into the strong electronic overlap category. This contrasts, however, with the strong inhibiting effect of BF_4^- although BF_4 is a weaker ion pair former than ClO_4^-.[2] The order of anion effects shown in Fig. 3 is at significant variance with the ion-pairing tendency of anions in MeCN solutions, reported[2] to increase in the order PF_6 $<BF_4$ $<ClO_4$ $<CF_3SO_3$. These differences in trends are reconciled by assuming that BF_4 and CF_3SO_3 are not only engaged in simple ion pairing, *i.e.*, outer-sphere complexation, but also tend to compete with (unfavourably) co-ordinated MeCN for an inner-sphere place [equation (5)].

$$\{Fe(dmf)_5(MeCN); X\}^{2+} \rightleftharpoons \{Fe(dmf)_5X; (MeCN)\}^{2+} \qquad (5)$$

Such anation equilibria could lower the driving force since π-back bonding MeCN stabilising the divalent state is withdrawn. Therefore, additional support for our suggestion is given by the decrease in conversion (in addition to the colour changes) when salt is added. Further work on these problems will be pursued. In the reaction between $[Fe(tmphen)_3]^{2+}$ and Fe^{3+}, on the other hand, this minor contribution cannot be resolved relative to the main anion effect of reducing the Coulombic repulsion of the positively charged reactant species.

In summary, the present paper provides new aspects to non-aqueous outer-sphere electron transfer. The change in reactivity in response to variations in the added electrolyte gives additional information relative to simple rate constants.

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