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Solvation and Reactivity in the Ferrocene–Ferricinium Electron Exchange Reaction

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Abstract

The remarkably small solvent effect on reactivity for the ferrocene–ferricinium electron exchange reaction, unexpected on the basis of Marcus's theory, is analysed into initial state and transition state contributions with the aid of published kinetic data and new solubility measurements. This analysis has been conducted on the basis of the tetraphenylarsonium–tetraphenylboronate (TATB) and ferrocene–ferricinium (fc/fc^+) assumptions.

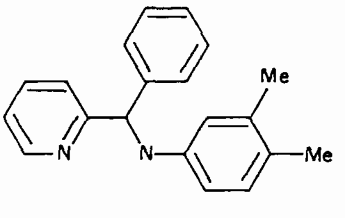
Introduction

There has been considerable progress in recent years in understanding solvent effects on reactivity of inorganic complexes in terms of solvation of initial and transition states [1], though the emphasis has been on substitution processes. For redox reactions, the Marcus–Hush theory of electron transfer [2] has been widely used in discussions of factors controlling reactivity, with a remarkable degree of success [3]. Incorporated within this theory, and explicit in the equations developed, is a dielectric term determining the solvent contribution. For simple outer-sphere electron transfer reactions between an uncharged complex and its 1+ or 1– analogue, where there is zero overall Gibbs free energy change and a zero charge product, the theory can be applied in a simple and straightforward manner. The dependence of rate constant on the dielectric parameter $(1/n^2 - 1/D_s)$, where n is the refractive index of the solvent ($n^2 = D_{op}$, its optical dielectric constant) and D_s is its static dielectric constant, can be predicted using reasonable values for such constants as the dimensions of reactants and of the transition state. Such reactions as the electron exchange between tris-(hexafluoroacetylacetonato)-ruthenium(III) and its ruthenium(II) analogue [4], and between bis-biphenylchromium(0) and its chromium(I) analogue [5], conform closely to the predictions of the Marcus–Hush theory.

On the other hand, the hexakis-cyclohexylisocyanidemanganese(II)/(I) [6a]** and ferrocene–ferricinium [7] electron exchange reactions do not conform with the Marcus–Hush theory predictions. Indeed rate constants for this latter reaction are very similar in almost all solvents studied. It is particularly disappointing that the ferrocene–ferricinium reaction does not conform to theoretical expectations, since this couple is often used as a reference for electrochemical measurements. We therefore decided to undertake an initial state–transition state analysis of solvent effects on reactivity for this ferrocene–ferricinium reaction, to see what light this might shed on the role of solvation here. In this paper we present the solubility measurements needed to establish transfer chemical potentials for the reactants, and thence analyse the published rate constants to separate solvent effects into initial state and transition state components.

Experimental

Ferrocene was prepared by the standard method [8] and purified by recrystallisation from cyclohexane and subsequent sublimation. Ferricinium hexafluorophosphate [9] and picrate [10] were prepared by published methods. The $[Fe(Me_2bsb)_3]^{2+}$ cation, $Me_2bsb = 1$, was generated from iron(II) chloride tetrahydrate, 2-benzoyl pyridine, and 3,4,-dimethylaniline [11], and precipitated as its iodide or hexafluorophosphate by the addition of the respective potassium salts after filtration of the



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**The variation in $\Delta V^{\neq}$ values with solvent for this and related reactions also indicates an unusual, complicated and subtle balance of solvent–solute interactions [6b].

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$[Fe(Me_2bsb)_3]^{2+}$-containing product solution through Celite to remove traces of oily material which generally accompanies its formation.

Solubilities were measured using methods described earlier [12]. The ferricinium cation undergoes slow reaction in dimethyl sulfoxide or acetonitrile solution, so solubilities were determined somewhat more rapidly in these media. Thermostatted agitation was carried out for about one hour, with minimal exposure to atmospheric oxygen. Concentrations of saturated solutions were determined by spectrophotometry or by atomic absorption spectrometry after appropriate dilution. Dilutions for measurements by the latter technique were effected with water; dilutions were sufficiently large for calibration of the instrument (Perkin-Elmer 1100B) by the appropriate aqueous standards. In view of the variation of the extinction coefficient of the ferricinium cation with solvent [13], and indeed the wide variation of the reported value for aqueous solution between observers [13, 14], we determined the extinction coefficient in each solvent by absorbance measurements (Unicam SP8-100 spectrophotometry) on solutions of known concentration (weighing, followed by atomic absorption check of concentration).

Results

Measured solubilities are recorded in Table 1, together with an indication as to whether they were recorded by atomic absorption or by ultraviolet–visible spectrometry. We have omitted the solubility of ferrocene in water from our reported results. In the present investigation we obtained a value of 1.6×10^{-4} mol dm^{-3} (at 298.2 K), which agrees fairly well with Brisset's published value [18]. Previously we estimated a rather higher value [19]; the results of radiation studies of ferricinium salts suggest

TABLE 1. Solubilities and transfer chemical potentials (the former in mol dm^{-3}, the latter in kJ mol^{-1}; in all cases at 298.2 K; transfer from water except where indicated otherwise)

	H_2O	MeOH	MeCN	$MeNO_2$	Me_2CO	Me_2SO	$PhNO_2$
$[Fe(Me_2bsb)_3]I_2$							
abs. sat. soln.[a]	4.36	707	2340	3150	1240		3020
$\delta_m\mu^\theta$ (salt)		−37.9	−46.8	−49.0	−42.1		−49.7
$2\delta_m\mu^\theta$ (I^-)[b]		14.6	33.6	34.0	50.0		36.0
$\delta_m\mu^\theta$ (cation)		−52.5[c]	−79.6	−83.0	−92.1		−84.7
$[Fe(Me_2bsb)_3](PF_6)_2$							
abs. sat. soln.	0.052	17.0	2310	1880	2100		1820
$\delta_m\mu^\theta$ (salt)		−43.1	−79.6	−78.1	−78.9		−77.8
$\delta_m\mu^\theta$ (PF_6^-)		4.7[d]	0	2.5	6.6	4.7[e]	3.5
$[Fe(cp)_2](PF_6)$							
10^3 conc. sat. soln.[f]	9.9	27	466	552	396	1140	222
$\delta_m\mu^\theta$ (salt)		−5.0	−19.1	−19.9	−18.3	−23.5	−15.4
$\delta_m\mu^\theta$ (fc^+)		−9.7	−19.1	−22.4	−24.9	−28.2	−18.8
conc. sat. soln. (ppm)[g]	640	1875				12000	
$\delta_m\mu^\theta$ (fc^+)		−10.0				−26	
$[Fe(cp)_2](pic)$							
10^3 conc. sat. soln.[f]	4.8	94					398
$\delta_m\mu^\theta$ (salt)		−14.7					−21.9
$\delta_m\mu^\theta$ (pic)[b]		−6					−5
$\delta_m\mu^\theta$ (fc^+)		−9					−17
$[Fe(cp)_2]$							
abs. satd. soln.[h]		6.7	13.2	13.8	27.0	18.9	212
$\delta_m\mu^\theta$ (fc)[i]		j	−1.7[k]	−1.8	−3.5	−2.6[k]	−8.6
$\delta_m\mu^\theta$ (initial state)[i]			−11.1	−14.5	−18.7	−21.1	−17.7
$\delta_m\Delta G^{\neq}$[l]			0.3	0	0.6	3.2	2.3
$\delta_m\mu^{\theta\ddagger}$[i]			−10.8	−14.5	−18.1	−17.9	−15.4

[a] Absorbance of saturated solution (allowing for dilution) ($\epsilon(580) = 13\,000$ for this cation [15]). [b] From ref. 16. [c] Agrees with $\delta_m\mu^\theta$ values obtained earlier via solubility of perchlorate salt [15]. [d] Consistent with trends for water–methanol reported in ref. 17. [e] From atomic emission determination of KPF_6 solubility. [f] Allowing for solvent effect on ϵ for the fc^+ cation (refs. 13 and 14). [g] Determined by atomic absorption spectrometry. [h] $\epsilon(490) = 91$ (ref. 13). [i] For transfer from methanol. [j] $\delta_m\mu^\theta$ (ferrocene; MeOH → water) > 15 kJ mol^{-1}. [k] Transfer chemical potentials agree with those reported earlier in ref. 18. [l] Calculated from the rate constants reported in ref. 7.

that all of these direct solubility measurements actually involve colloidal solutions or very fine suspensions [20], which would give erroneously high values by atomic absorption or by ultraviolet–visible spectroscopy.

Discussion

Transfer chemical potentials for the various salts and for ferrocene were calculated in the usual way, in all cases assuming that the ratios of activity coefficients in the non-aqueous solvents to those in water are unity. The solubilities of the salts in some of the solvents were uncomfortably high for this assumption, though in the derivation of $\delta_m\mu^\theta$ (PF_6^-) using the $[Fe(Me_2bsb)_3]^{2+}$ cation deviations from this assumption should cancel out. In any case both this and the $[Fe(cp)_2]^+$ cation are large cations of low charge. Diggle and Parker's radius for $[Fe(cp)_2]^+$ leads to a low K_{ip} [21]; conductivity measurements of Wahl *et al.* [7] indicate little ion-pairing in the solvents used in his kinetic study. The agreement between the estimated values for $\delta_m\mu^\theta$ ($[Fe(cp)_2]^+$) via $[Fe(Me_2bsb)_3]^{2+}$ and via $[Fe(cp)_2]$[picrate] is good in the two cases (involving three solvents) checked. In view of the doubts expressed in the 'Results' concerning the solubility of ferrocene in water, we have given $\delta_m\mu^\theta$ values in Table 1 with respect to transfer from methanol. Where relevant, our solubilities and transfer chemical potentials for ferrocene agree with published data [18]. The use of methanol rather than water for reference solvent is no disadvantage in the present paper, since there are no kinetic data available for ferrocene–ferricinium electron transfer in aqueous solution.

The very large negative values for $\delta_m\mu^\theta$ ($[Fe(Me_2bsb)_3]^{2+}$) (Table 1) are consistent with its well-established high hydrophobicity [22]. Indeed they correlate well with those for tetramethyltin and for tetraethyltin [23], though values for this iron complex are approximately twice those for the tetraalkyltin compounds. Transfer of $[Fe(cp)_2]^+$ from water to organic solvents is also favourable, as expected, though $\delta_m\mu^\theta$ values are considerably smaller than for the $[Fe(Me_2bsb)_3]^{2+}$ cation. However trends in $\delta_m\mu^\theta$ values for these two cations are parallel, suggesting similar solute–solvent interactions. The PF_6^- anion is destabilised much less than iodide on transfer from water into the solvents included in Table 1. The differences are larger than expected simply from the respective ionic radii, so it seems probable that hydrogen-bonding to varying extents is affecting the $\delta_m\mu^\theta$ (PF_6^-) values.

The rate constant for electron transfer from ferrocene to ferricinium hardly varies with the dielectric properties of the medium, which will have little effect on the ease of approach previous to the electron transfer step. An initial state–transition state analysis of this small solvent effect on reactivity is included in Table 1. This uses the kinetic data of Wahl *et al.* [7], is based on methanol as the reference solvent (since such data are unobtainable in water) and uses the TATB single ion extrathermodynamic assumption [24] in the derivation of transfer chemical potentials for the ferricinium ion and for the transition state. The results of this analysis are depicted in Fig. 1. Because there is such a small solvent effect on electron exchange rate constants in this system the initial and transition states perforce move almost in parallel. However each covers a range of nearly 20 kJ mol^{-1} over the solvents studied. As the activation barrier in methanol is only 34.4 kJ mol^{-1}, this means that the lack of a marked solvent effect on the kinetics is concealing large but almost identical solvent effects on the initial state and the transition state. This is not a common situation, though it has also been reported for substitution in pentacyanoferrates(II) [25], where, as here, the transition state bears a particularly close resemblance

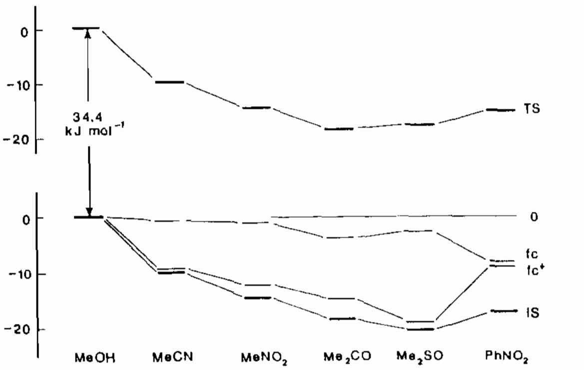

Fig. 1. Initial state–transition analysis for the ferrocene–ferricinium electron exchange reaction according to the TATB assumption (kJ mol^{-1}; molar scale; 298.2 K).

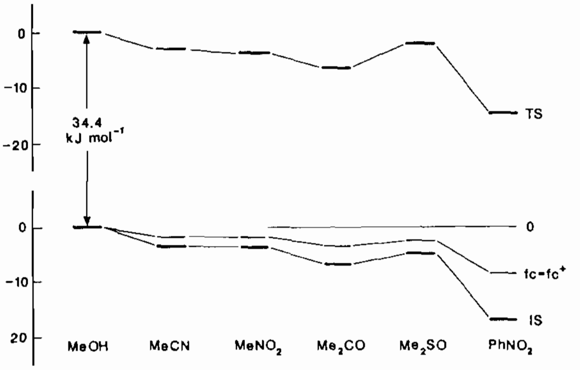

Fig. 2. Initial state–transition analysis for the ferrocene–ferricinium electron exchange reaction according to the fc/fc⁺ assumption (kJ mol^{-1}; molar scale; 298.2 K).

to the initial state. For the ferrocene–ferricinium reaction, divergence between initial and transition state trends is most marked, as might be expected, where solvation is heaviest, and most extrusion of solvating solvent is needed to permit close approach of the two reactants for electron transfer.

In view of the popularity of the ferrocene–ferricinium single ion extrathermodynamic assumption we also present, in Fig. 2, the results of an initial state–transition state analysis of solvent effects on reactivity for the electron transfer reaction involving these two species. The general features of this analysis are, fortunately, fairly similar to the TATB-based analysis of Fig. 1 and Table 1. Again the small solvent effect on kinetics hides larger solvent effects on reactants and transition states, but these latter are rather less pronounced according to the ferrocene–ferricinium assumption than according to the TATB assumption. The only real difference between the TATB and the fc/fc$^+$ Figures is the transfer from dimethyl sulfoxide to nitrobenzene. Deductions according to the two assumptions might be expected to show more worrying differences had it been possible to include water in our considerations [21].

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References

1 M. J. Blandamer and J. Burgess, *Coord. Chem. Rev., 31* (1980) 93; *Pure Appl. Chem., 51* (1979) 2087; *54* (1982) 2285; *55* (1983) 55.
2 R. A. Marcus, *J. Chem. Phys., 24* (1956) 966, 979; N. S. Hush, *Prog. Inorg. Chem., 8* (1967) 391.
3 R. D. Cannon, *Electron Transfer Reactions*, Butterworths, London, 1980.
4 M.-S. Chan and A. C. Wahl, *J. Phys. Chem., 86* (1982) 126.
5 T. T.-T. Li and C. H. Brubaker, *J. Organomet. Chem., 216* (1981) 223; T. T.-T. Li, M. J. Weaver and C. H. Brubaker, *J. Am. Chem. Soc., 104* (1982) 2381; M. J. Weaver and T. Gennett, *Chem. Phys. Lett., 113* (1985) 213; J. R. Eyler and D. E. Richardson, *J. Am. Chem. Soc., 107* (1985) 6130.
6 (a) R. M. Nielson and S. Wherland, *Inorg. Chem., 23* (1984) 1338; (b) M. Stebler, R. M. Nielson, W. F. Siems, J. P. Hunt, H. W. Dodgen and S. Wherland, *Inorg. Chem., 27* (1988) 2893.
7 E. S. Yang, M.-S. Chan and A. C. Wahl, *J. Phys. Chem., 84* (1980) 3094.
8 G. Wilkinson, *Org. Synth., Collective Vol. 4* (1963) 473.
9 E. S. Yang, M.-S. Chan and A. C. Wahl, *J. Phys. Chem., 79* (1975) 2049.
10 I. M. Kolthoff and F. G. Thomas, *J. Phys. Chem., 69* (1965) 3049.
11 P. Krumholz, *Inorg. Chem., 4* (1965) 609.
12 M. J. Blandamer, J. Burgess, B. Clark, P. P. Duce, A. W. Hakin, N. Gosal, S. Radulović, P. Guardado, F. Sanchez, C. D. Hubbard and E. A. Abu-Gharib, *J. Chem. Soc., Faraday Trans. I, 82* (1986) 1471.
13 G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, *J. Am. Chem. Soc., 74* (1952) 2125.
14 Y. S. Sohn, D. M. Hendrickson and H. B. Gray, *J. Am. Chem. Soc., 92* (1970) 3233; A. Horsfield and A. Wassermann, *J. Chem. Soc., Dalton Trans.,* (1972) 187; M. D. Rowe and A. J. McCaffery, *J. Chem. Phys., 59* (1973) 3786.
15 J. Burgess and C. D. Hubbard, *J. Chem. Soc., Chem. Commun.,* (1983) 1482.
16 Y. Marcus, *Ion Solvation*, Wiley, New York, 1985, pp. 168–169.
17 M. J. Blandamer, J. Burgess, J. Fawcett, S. Radulović and D. R. Russell, *Transition Met. Chem., 13* (1988) 120.
18 J.-L. Brisset, *J. Chem. Eng. Data, 27* (1982) 153.
19 E. Pelizzetti, E. Pramauro, M. J. Blandamer, J. Burgess and N. Gosal, *Inorg. Chim. Acta, 102* (1985) 163.
20 G. S. Laurence, personal communication.
21 J. W. Diggle and A. J. Parker, *Electrochim. Acta, 18* (1973) 975.
22 J. Burgess and C. D. Hubbard, *J. Am. Chem. Soc., 106* (1984) 1717.
23 M. H. Abraham, *J. Chem. Soc., Perkin Trans. II,* (1972) 1343.
24 A. J. Parker, *Chem. Rev., 69* (1969) 1.
25 M. J. Blandamer, J. Burgess, K. W. Morcom and R. Sherry, *Transition Met. Chem., 8* (1983) 354.