# Solvation and Reactivity of Iron(II)–Diimine Complexes in Dimethyl Sulfoxide–Water Mixtures

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Kinetics of the base hydrolysis of several iron(II)-diimine complexes, including two with terdentate ligands and one with an encapsulating ligand, and of the peroxodisulfate oxidation of three ternary iron(II)-diimine-cyanide complexes, are reported for reaction in dimethyl sulfoxide (DMSO)-water mixtures at 298.15 K. Solubilities of simple and complex salts have been determined in these mixtures, both to extend the range of simple and complex ion-transfer chemical potentials and to provide the basis for initial-state/transition-state analyses of reactivity trends for several of the base hydrolysis and peroxodisulfate oxidations. Cases are identified where the destabilisation of hydroxide ions, OH<sup>-</sup>(aq), by added DMSO increases the rate of base hydrolysis. We also identify cases where compensation effects result in only a small change in rate constant for oxidation by peroxodisulfate where DMSO is added.

For many years we have been interested in reactivity trends for substitution and redox reactions of inorganic complexes in binary aqueous solvent mixtures.<sup>1</sup> More recently, we have established trends in transfer chemical potentials for a variety of inorganic ions and complexes in several series of binary aqueous mixtures, with particular concern to use these data to analyse solvent effects on reactivity trends into initial-state and transition-state contributions. Most of our investigations have involved co-solvents such as methanol,<sup>2</sup> ethanol,<sup>3</sup> propanone<sup>4</sup> and propan-2-ol.<sup>5,6</sup>

Related studies<sup>7</sup> have involved the dipolar protic solvent dimethyl sulfoxide. The properties of the binary mixture, DMSO-water set it apart from the aqueous mixtures just mentioned.<sup>8</sup>' For example, the excess molar Gibbs energies and enthalpies of mixing are negative,<sup>9</sup> pointing to strong inter-component interactions.<sup>10</sup>

In this paper we report and discuss kinetic and thermodynamic results for solutions using this co-solvent in aqueous mixtures with particular reference to inorganic solutes, mainly iron(II) complexes. An interesting link is therefore established with the classic studies of Tommila and coworkers (e.g. ref. 11) into the kinetics of reactions involving organic substrates in this mixture. We describe reactivity trends for base hydrolysis and for peroxodisulfate oxidation of a selection of low-spin iron(II) complexes. We report the results of solubility measurements on appropriate salts of these complexes and on other salts for which solubility data are required in order to build up a picture of transfer chemical potentials for these iron(II) complexes in the context of the general pattern for inorganic substances. We are than able to analyse our reactivity patterns into initial-state and transition-state contributions. The latter are based on the TATB extrathermodynamic assumption<sup>12,13</sup> which equates the transfer chemical potentials of  $Ph_4As^+$  and  $Ph_4B^-$  ions;

 $\Delta(aq \rightarrow x_2)\mu^0(Ph_4 As^+;$ 

sln; concentration scale; 298.2 K)

 $= \Delta(\mathrm{aq} \to x_2) \mu^0(\mathrm{Ph}_4\mathrm{B}^-;$ 

sln; concentration scale; 298.2 K) (1)

There are strong arguments in favour of the technique of combining kinetic and solubility data along the lines described here and in previous publications from this laboratory.<sup>1-5</sup> For example, we show how modest dependences of rate constants on solvent composition can mask quite striking dependences of standard chemical potentials on composition for intial and transition states.

## Experimental

Solvent

The composition of the binary aqueous mixture is reported either in terms of mole fraction  $x_2$  where liquid 2 = DMSO and liquid 1 = water, or in terms of vol.% (id) DMSO. The latter refers to the volumes of water and DMSO before mixing as used in the preparation of a given solvent mixture.

# **Preparation of Complexes**

The various iron(II) complexes were prepared using standard procedures. Solutions containing tris(1,10-phenanthroline) iron(II) were generated by adding a slight excess of the ligand to iron(II) ammonium sulfate in aqueous solution. The trisbidentate and bis-terdentate iron(II) complexes were made using Krumholz's method<sup>14</sup> from 2-benzoylpyridine or 2,6diacetylpyridine plus the appropriate amine in aqueous ethanol solutions in the presence of iron(II) chloride or iron(II) ammonium sulfate; the iron(II) complexes were precipitated their perchlorate salts. An encapsulated complex as [Fe(cage)]<sup>2+</sup> (see Appendix) was prepared from iron(II) chloride, dimethylglyoxime, and boric acid by the established method.<sup>15</sup> The ternary iron(II)-diimine-cyanide complexes were made using Schilt's method<sup>16</sup> from the respective trisdiimine iron(II) cation, except for  $[Fe(CN)_4(HN =$ CHCH=NH)]<sup>2-</sup>, which was prepared from the ethane-1,2 diamine complex,  $[Fe(CN)_4(H_2NCH_2CH_2NH)]^{2-}$ , by air oxidation.17

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# Kinetics

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# Results

Chemical reactions were followed spectrophotometrically The ligands involved in the base hydrolysis and perthrough the decrease in absorbance with time at the  $v_{max}$  in oxodisulfate oxidation kinetics and in the solubility determithe UV-VIS region appropriate to each iron-diimine and nations are shown in the Appendix. The abbreviations used iron-diimine-cyanide complex. The kinetic data were here are also indicated in the Appendix. In almost all cases obtained using either a Unicam SP-1800 spectrophotometer the solvent mixtures contain  $\ge 40\%$  water by volume and linked to an IBM PC or a Hewlett-Packard HP8451A diode therefore at the reagent concentrations used in the kinetic array spectrophotometer with built-in HP 85 minicomputer. study, complications from ion-pair formation can be dis-Absorbances were recorded for at least 2.5 half-lives and used counted. as input data to the computers which calculated rate con-

# **Base Hydrolysis**

A summary of our results is reported in Table 1; these results extend previous data in several respects. The dependence of the second-order rate constants for hydroxide attack at iron(II)-diimine complexes on solvent compositions in DMSO-water mixtures has previously been reported for the complexes  $[Fe(bipy)_3]^{2+}$ ,  $[Fe(L^3)_3]^{4-}$ ,  $[Fe(L^5)_3]^{2+}$  and  $[Fe(L^1)]^{2+}$ , where the ligands L are as shown in the Appendix.

Table 1 First-order rate constant and derived second-order rate constants for the base hydrolysis of iron(n)-diffine complexes in DMSO-water mixtures<sup>a</sup>

(a)  $[Fe(phen)_3]^{2+}$ 

described by Moore.18

Solubilities

bilities.

stants using a least-squares procedure based on the method

Solubilities of iron(II) complexes were determined using the

procedures described.<sup>2</sup> All aliquots of equilibrated solutions

were diluted with water (>99%) and the dependences of  $\varepsilon_{max}$ 

on solvent composition were ignored in calculating the solu-

				k <sub>obs</sub> /10	<sup>-5</sup> s <sup>-1</sup>				<u></u>	
vol.% (id) DMSO	0.05 <sup>b</sup> 0.10 <sup>b</sup> 0.15 <sup>b</sup>		5*	0.20*	0.26 <sup>b</sup>		$k_2/10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$			
0 10 20 30 40	60 67 110 160 290		114 150 220 350 560	170 230 340 540 860		230 310 460 750 1170	300		120 150 230 380 580	
(b) $[Fe(L^6)_2]^{2+}$										
				$k_{obs}/1$	$0^{-5} s^{-1}$					
vol.% (id) DMSO	0.033 <sup>b</sup>	0.05 <sup>b</sup>	0.067 <sup>b</sup>	0.10 <sup>b</sup>	0.120 <sup>b</sup>	0.133 <sup>b</sup>	0.180 <sup>b</sup>	0.20 <sup>b</sup>	$k_2/10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	
0 20	53	16	81	48	66	84 147	126	222	80 120	
(c) $[Fe(L^7)_2]^{2+1}$	_									
				$k_{obs}/1$	$0^{-5} \mathrm{s}^{-1}$					
vol.% (id) DMSO	0.001 <sup>b</sup>	0.033 <sup>b</sup>	0.60 <sup>b</sup>	0.10 <sup>b</sup>	0.130 <sup>b</sup>	0.20 <sup>b</sup>	0.26*	0.30*	$k_2/10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	
0 40 60 70 <sup>c</sup> 80 <sup>c</sup>	46	2.8	3.9	110 1630 2890	6.8	8.4	10.9	0.18 14 135	4.6 30	
(d) $[Fe(cage)]^{2+}$						_				
	1 10			$k_{\rm obs}/10$	$0^{-5} s^{-1}$					
vol.% (id) DMSO	(	0.10 <sup>b</sup>	0.15 <sup>b</sup>	0.20 <sup>b</sup>		0.25 <sup>b</sup>	0.33 <sup>b</sup>		$k_2/10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	
0 10 20 40 50 70 80		3.6 1.3	4.3 1.7	6.1		7.7	9.4 5.9 5.7 4.5 3.4 5.4 7 9		2.9 1.8 1.7 1.4 1.0 1.6 2.4	

<sup>a</sup> At 298.2 K;  $I = 0.33 \text{ mol dm}^{-3}$  (NaCl). <sup>b</sup> [OH<sup>-</sup>]/mol dm<sup>-3</sup>. <sup>c</sup> in Bu<sub>4</sub>NOH-Et<sub>4</sub>NCl. <sup>d</sup>  $k_{obs}/s^{-1} = 2.3 \times 10^{-5}$  in Bu<sub>4</sub>NOH (aqueous; 0.33 mol dm<sup>-3</sup>).

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In the case of the bipy,  $L^5$  and  $L^1$  complexes, steadily increasing rate constants as the mole fraction of DMSO in the solvent mixture increased were attributed mainly to the steadily increasing standard chemical potential of hydroxide ions. Indeed, the trend for the bipy complex could be attributed almost entirely to this destabilisation of OH<sup>-</sup> ions. The situation with respect to anionic  $[Fe(L^3)_3]^{4-}$  complex ions was different; a decrease in reactivity was observed with increasing DMSO content. The kinetic pattern was more complicated, with significant rate law terms in the square and higher powers of hydroxide concentration. The interpretation was complicated by the possibility of hydroxide attack at the (activated) ligand rather than directly at the ion

$$-\{d[complex]/dt\} = k_2[OH^-] + k_3[OH^-]^2 + k_4[OH^-]^3 + \cdots$$
(2)

We have extended our kinetic data in three ways. For the bipy complex, we obtained results for reaction in mixtures richer in DMSO than previously reported. For a selection of other complexes, including some encapsulated species, we have determined second-order rate constants  $k_2$  as a function of DMSO content. For some other complexes, particularly a few very stable and inert cage complexes, we used the increased standard chemical potential of hydroxide ions in DMSO-rich mixtures to obtain kinetic data for reactions which are too slow for practical purposes in aqueous media at 298 K. Results in the last category are rather fragmented and will be reported elsewhere.<sup>19</sup> Results for the second category are reported in Table 1, which also includes experimental first-order rate constants  $k_{obs}$  (where  $[OH^-] \ge [Fe^{II}]$ complex]) and derived second-order rate constants  $k_2$ . For  $[Fe(bipy)_3]^{2+}$ ,  $k_{obs}$  in Bu<sub>4</sub>NOH (solution; 0.001 mol dm<sup>-3</sup>; ionic strength I = 0.33 mol dm<sup>-3</sup> using Et<sub>4</sub>NCl) increases from  $9 \times 10^{-4}$  s<sup>-1</sup> in 60% DMSO through  $27 \times 10^{-4}$  and  $84 \times 10^{-4}$  s<sup>-1</sup> in 80 and 90% DMSO to  $300 \times 10^{-4}$  in 100% DMSO. Technical difficulties prevented confirmation of a second-order rate law with negligible parallel solvolysis. Nonetheless, these results suggest a similar rapid increase in the rate of hydroxide attack in mixtures having high DMSO contents to those detailed in Table 1. Increases in rate constant with increase in DMSO content for various complexes are compared in Fig. 1.



**Fig. 1** Dependence of log  $[k_2(x_2)/k_2 \text{ (aq)}]$  for alkaline hydrolysis of several iron(11) complexes on composition of DMSO-water mixtures;  $k_2(x_2) = \text{rate constant in the mixture mole fraction of DMSO, } x_2$  whereas  $k_2(\text{aq}) = \text{rate constant for alkaline hydrolysis in aqueous solution. For key to ligands see the Appendix. Curves (a) and (b) use as reference solvent a DMSO-water mixture containing 40 vol.% DMSO.$ 

**Table 2** First-order rate constant  $k_{obs}$  for peroxodisulfate oxidation of iron(11)-diimine complexes in DMSO-water mixtures<sup>a</sup>

	$k_{\rm obs}/10^{-4} {\rm s}^{-1}$						
complex	0*	20 <sup>b</sup>	40 <sup>b</sup>	60 <sup>b</sup>			
$[Fe(CN)_{2}(bipy)_{2}]$ $[Fe(CN)_{4}(bipy)]^{2-}$ $[Fe(CN)_{4}(L^{5})]^{2-}$	65 26 21	22 21 120	4.6 12.7 230	0.62 9.2 25			

<sup>a</sup> At 298.2 K;  $[K_2S_2O_8]/mol dm^{-3} = 0.02$ ;  $[complex] \approx 10^{-4} mol dm^{-3}$ ;  $[Na_2 edta] = 10^{-5} mol dm^{-3}$ . <sup>b</sup> vol.% (id) DMSO.

#### Peroxodisulfate Oxidation

Peroxodisulfate oxidises ternary iron(II)-diimine-cyanide complexes to the analogous iron(II) complexes; these reactions obey a simple second-order rate law. Table 2 presents observed first-order rate constants for three such reactions carried out in mixtures containing 0, 20, 40 and 60% by volume (id) DMSO; the peroxodisulfate was present in large excess in each kinetic run. Initial concentrations of the complexes were in the range  $1 \times 10^{-4}$  to  $5 \times 10^{-4}$  mol dm<sup>-3</sup>.

# Solubilities and Transfer Chemical Potentials

We have measured the solubilities of several inorganic compounds in water–DMSO mixtures at 298 K in order to calculate their transfer chemical potentials and thence estimate transfer chemical potentials for the constituent ions. These data both supplement and complement published single-ion transfer properties and enable us to carry out initial state/ transition state dissections of observed reactivity patterns of the type documented in Tables 1 and 2. In Table 3 we report solubilities (with a check on KPF<sub>6</sub> solubility in water<sup>20</sup>) and derived transfer chemical potentials (TATB assumption<sup>21</sup>) for the compounds examined in this study.

#### Discussion

# Trends in the Kinetics of Base Hydrolysis

Fig. 1 illustrates the kinetic pattern for a series of iron(II)diimine complexes. The different gradients and shapes of the plots for the various complexes shows that the nature of the ligand plays an important role in determining reactivity in DMSO-water mixtures. Clearly, the apparently dominant role of the transfer chemical potentials for hydroxide ions in determining the pattern in the rate constants for the base hydrolysis of [Fe(bipy)<sub>3</sub>]<sup>2+</sup> (cf. Fig. 2 of ref. 22) was coincidental rather than general. The flattening out of all three curves, for the bipy,  $L^7$  and cage complexes in Fig. 1 at high DMSO mole fractions is not what one would predict from the known variation of  $\Delta(aq \rightarrow x_2)\mu^0(OH^-)$  over the whole DMSO-water composition range. We return to these kinetic results in the section below where we consider the dependences on solvent composition of the initial state and transition state and the solvent effects on the rate constants for peroxodisulfate oxidation.

#### **Transfer Chemical Potentials**

Fig. 2 shows the trends in transfer chemical potentials of binary iron(II)-diimine and ternary iron(II)-diimine-cyanide complexes as determined in this and related investigations. The pattern accords with expectation and can be rationalised in terms of hydrophobicity/lipophobicity of diimine or other

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Table 3 Measured solubilities and derived transfer chemical potentials for inorganic compounds in DMSO-water mixtures at 298.15 K<sup>a</sup>

	vol.% (id) DMSO								
	0	10	20	30	40	50	60	80	100
$ \frac{\text{KPE}_{6}}{\text{sol}^{a,b}} \\ \Delta(\text{salt})^{a} \\ \Delta(K^{+})^{d} \\ \Delta(\text{PF}_{6}^{-}) $	0.49 <sup>c</sup>		0.67 - 1.6 - 0.3 - 1.3		1.04 - 3.8 - 1.6 - 2.2	<u></u>	1.41 - 5.3 - 3.4 - 1.9	2.05 -7.1 -7.3 0.2	2.18 7.4 12.1 4.7
$[Fe(L6)2](PF6)2ASSe\Delta(salt)\Delta(complex)$	6.0		21.8 9.6 7.0		116 22 18		219 -27 -23		
$[Fe(L7)2](PF6)2ASS\Delta(salt)\Delta(complex)$	2.67		12.9 11.7 9.1		122 28 24				
$[Fe(L1)](ClO_4)_2$ ASS $\Delta(salt)$ $2\Delta(ClO_4^-)^f$ $\Delta(complex)$	216	260 - 1.4 + 0.7 - 2.1	390 - 4.4 + 1.4 - 5.8		480 5.9 + 2.6 8.5				
$K_2[Fe(CN)_4(ein)]$ $\Delta(salt)$ $\Delta(complex)$			4.1 4.7		7.4 10.5		12.2 18.9		
$K_2[Fe(CN)_4(bipy)]$ $\Delta(salt)$ $\Delta(complex)$			2.6 3.2		13.1 16.2		21.2 30		33.8 60
$K_2[Fe(CN)_4(phen)]$ $\Delta(salt)$ $\Delta(complex)$			1.8 1.2		8.1 11.2		17.8 25		
$K_2[Fe(CN)_4(L^5)]$ Δ(salt Δ(complex)			$-0.5 \\ 0.1$		-2.0 1.1		-4.7 2.0		2.2 28
$[Fe(CN)_2(bipy)_2] \\ \Delta(complex)$			- 3.8		- 5.6		- 8.0	- 10.4	- 10.2

<sup>*a*</sup> sol = solubility/mol dm<sup>-3</sup>;  $\Delta$  (salt) =  $\Delta(aq \rightarrow x_2) \mu^0$ (salt; sln; concentration scale)/kJ mol<sup>-1</sup>;  $\Delta(ion) = \Delta(aq \rightarrow x_2) \mu^0(ion; sln; concentration scale)/kJ mol<sup>-1</sup>.$ *e.g.* $<math>\Delta(KCl) = \Delta(K^+) + \Delta(Cl^-)$  meaning that:  $\Delta(aq \rightarrow x_2) \mu^0(KCl; sln; concentration scale)/kJ mol<sup>-1</sup> = <math>\Delta(aq \rightarrow x_2) \mu^0(K^+; sln; concentration scale)/kJ mol<sup>-1</sup> + <math>\Delta(aq \rightarrow x_2) \mu^0(Cl^-; sln; concentration scale)/kJ mol<sup>-1</sup>. Transfer chemical potentials for ions calculated using the TATB assumption. <sup>$ *b*</sup> By atomic absorption spectroscopy (Perkin-Elmer 1100B). <sup>*c*</sup> cf. 0.432 at room temperature (ref. 20). <sup>*d*</sup> Ref. 21. <sup>*e*</sup> Absorbance of saturated solution,*i.e.*measured absorbance × dilution. <sup>*f*</sup> From ref. 4.



Fig. 2 Dependence of single-ion transfer parameters on vol.% DMSO in DMSO-water mixtures for several iron(11) complexes at 298.2 K

ligands and the strong hydrophilicity of cyanide ligands. Electrostriction effects play only a minor role. Fig. 3 includes a few of these results placed in the general context of transfer chemical potentials of inorganic ions, simple cations and anions, and complexes in DMSO-water mixtures. Again a consistent and intuitively reasonable pattern can be seen; ionic charge-solvent permittivity interactions play an important role particularly for the small (monoatomic) ions. It is noteworthy that hydroxide ions are the most destabilised of all simple anions when DMSO is added.

A comparison of the transfer chemical potentials for the  $[Fe(phen)_3]^{2+}$  cation serves as an example of how such trends when DMSO is the co-solvent fit into the pattern for transfer parameters in alcohol-water mixtures (Fig. 4). More interesting is the pattern for the ternary complex  $[Fe(CN)_2(bipy)_2]$  shown in Fig. 5. The minimum and inflections attributable to solvent structural effects in alcohol-water mixtures are notably absent from the DMSO-water plot in this figure. In the latter case, the plot is a smooth curve of the type expected where the phenomenon of simple preferential solvation is present, presumably by the organic co-solvent of the bipy ligand. Unfortunately, it is not possible to obtain the curve covering the complete range of solvent compositions to 100% DMSO because in DMSO and DMSO-rich mixtures the solid phase is no longer the tri-



Fig. 3 Dependence of transfer chemical potentials for various ions in DMSO-water mixtures as a function of vol.% DMSO at 298.2 K

hydrate which is in equilibrium with, and crystallises from, water-rich mixtures.

# Initial State-Transition State Analysis: Base Hydrolysis

The analysis has been carried out for three complexes (Table 4). The results are depicted for two of these complexes in Figs. 6 and 7. The pattern for the phen complex is similar to that for the  $L^6$  complex; the particular feature of this system is the close compensation of the stabilisation of  $[Fe(phen)_3]^{2+}$  and the destabilisation of OH<sup>-</sup> ions as the proportion of DMSO in the mixture increases. In fact, the slightly greater stabilisation of  $[Fe(L^6)_2]^{2+}$  than of  $[Fe(phen)_3]^{2+}$  means that the initial state for the reaction between OH<sup>-</sup> and  $[Fe(L^6)_2]^{2+}$  is moderately stabilised on addition of DMSO. The small increase in rate constant emerges from a slightly greater stabilisation of the transition state. Conversely the initial state for the reaction between [Fe(cage)]<sup>2+</sup> and OH<sup>-</sup> is destabilised markedly on addition of DMSO (hydroxide destabilisation dominant), with the transition state closely following the initial state. The relative solvent effects on initial and transition states are clear from the presentation in Fig. 6. However, this figure gives no impression of the relation of these changes to the activation



**Fig. 4** Dependence of transfer chemical potentials of the iron(II) complex  $[Fe(phen)_3]^{2+}$  on mole fraction  $x_2$  of organic co-solvent at 298.2 K for the binary aqueous mixtures (a) methanol, (b) ethanol, (c) DMSO, (d) propan-2-ol and (e) tert-butyl alcohol



Fig. 5 Dependence of transfer chemical potential for the iron(II) complex  $[Fe(CN)_2(bipy)_2]$  on mole fraction,  $x_2$  organic co-solvent in the binary aqueous mixtures (a) methanol, (b) ethanol, (c) DMSO, (d) propan-2-ol, (e) tert-butyl alcohol and (f) propanone

barrier. This relation is clear from the alternative style of presentation in Fig. 7. This figure shows that, at least for the reaction between  $[Fe(cage)]^{2+}$  and  $OH^-$  ions, on going from solutions in water to solutions in 80% DMSO, there is an increase of about 40% in the chemical potentials of transition state. This is, in fact, one of the largest increases for transition states in the case of reactions in binary aqueous mixtures. Remarkably, this large effect is associated with only a very small change in rate constant. Here we have an example of large solvent effects on initial and transition states largely compensating to give an almost negligible resultant solvent effect on reactivity. In this respect, the present reaction behaves very similarly to substitution in pentacyano-ferrate(II).<sup>23</sup>

**Table 4** Initial state-transition state analysis of reactivity trends for the base hydrolysis of iron(n)-diimine complexes in DMSO-water mixtures<sup>a</sup>

	vol.% (id) DMSO					
	0	20	40	60	80	
$[Fe(phen)_3]^{2+}$ $k_2$ $\Delta\Delta^{\neq}G$ $\Delta(complex)$ $\Delta(OH^{-})$ $\Delta(is)$ $\Delta(\neq)$	12	23 1.6 7.0 5.1 1.9 3.5	$58 \\ -3.9 \\ -13.3 \\ 13.6 \\ 0.3 \\ -3.6$			
$[Fe(L^{6})_{2}]^{2+}$ $k_{2}$ $\Delta\Delta^{\neq}G$ $\Delta(complex)$ $\Delta(is)$ $\Delta(i \neq )$	5.2	11 1.9 7.0 1.9 3.8	26 -4.0 -17.2 -3.6 -7.6			
$[Fe(cage)]^{2+}$ $k_2$ $\Delta \Delta \neq G$ $\Delta(complex)$ $\Delta(OH^{-})$ $\Delta(is)$ $\Delta(\neq)$	3.32	1.75 1.6 -2.0 5.1 3.1 4.7	1.19 2.5 -3.6 13.6 10.0 12.5	0.98 3.0 - 5.4 27.7 22.3 25.3	2.36 0.8 -9.2 44.7 35.5 36.4	

<sup>a</sup> At 298 K;  $k_2$  is in  $10^{-3}$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>;  $\Delta \Delta^{*}G = \Delta(aq \rightarrow x_2)$  $\Delta^{*}G^{0}$ (solution; concentration scale)/kJ mol<sup>-1</sup>;  $\Delta$ (complex) =  $\Delta(aq \rightarrow x_2) \ \mu^{0}$ (complex; solution; concentration scale)/kJ mol<sup>-1</sup>;  $\Delta(OH^{-}) = \Delta(aq \rightarrow x_2) \ \mu^{0}$ (OH<sup>-</sup>; solution; concentration scale)/kJ mol<sup>-1</sup>;  $\Delta(is) = \Delta(aq \rightarrow x_2) \ \mu^{0}$ (initial state; solution; concentration scale)/kJ mol<sup>-1</sup> +  $\Delta(aq \rightarrow x_2) \ \mu^{0}$ (complex; solution; concentration scale)/kJ mol<sup>-1</sup>;  $\Delta(is) = \Delta(aq \rightarrow x_2) \ \mu^{0}$ (complex; solution; concentration scale)/kJ mol<sup>-1</sup>;  $\Delta(iq \rightarrow x_2) \ \mu^{0}$ (CM<sup>-</sup>; solution; concentration scale)/kJ mol<sup>-1</sup>;  $\Delta(iq \rightarrow x_2) \ \mu^{0}$ (CM<sup>-</sup>; solution; concentration scale)/kJ mol<sup>-1</sup>;  $\Delta(iq \rightarrow x_2) \ \mu^{0}$ (transition state; solution; concentration; concentration scale)/kJ mol<sup>-1</sup>; single ion transfer parameters calculated using TATB assumption.

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Fig. 6 Comparison of the dependence of vol.% DMSO of the standard chemical potentials of hydroxide ions, initial states, transition states for the alkaline hydrolysis of (a)  $[Fe^{II}(L^6)_2]^{2+}$  and (b)  $[Fe(cage)]^{2+}$  ions; the plot for IS refers to the combined complex and OH<sup>-</sup> dependences

# Initial State–Transition State Analysis: Peroxodisulfate Oxidation

Details of this reaction are set out in Fig. 8. In each case the changes in rate constant are relatively small, so the standard chemical potentials of initial and transition states rise roughly in parallel as the proportion of DMSO in the reaction mixture increases. The rate of increase depends considerably on the nature of the iron(II) complex, reflecting the trends in transfer standard chemical potentials reported above. As in the case of the substitution reactions discussed above, the destabilisations are marked; for the reaction between  $[Fe(CN)_4(bipy)]^2$  and  $S_2O_8^2$  (sln), the destabilisation both of the initial state and the transition state are over half the magnitude of the activation barrier itself; Table 5. For all these complexes, large changes in standard chemical potentials for initial and transition states almost compensate, to provide another series of examples of large but almost equal effects on initial and transition states, resulting



Fig. 7 Comparison of the dependence on vol.% DMSO of the standard chemical potentials of hydroxide ions, initial states, transition state and the iron complex cation  $[Fe(cage)]^{2+}$ ; the plot for IS refers to the combined complex and OH<sup>-</sup> dependences



Fig. 8 Comparison of the dependences on vol.% DMSO of the standard chemical potentials of initial and transition states for the peroxodisulfate oxidation of iron(11)-cyanide-diimine complexes, for the peroxodisulfate anion and for  $[Fe(CN)_4(bipy)]^{2-}$ , dependences for transition state TS(*a*), initial state IS(*a*), complex Fe<sup>II</sup>(*a*); for  $[Fe(CN)_2(bipy)_2]$ , dependences for transition state TS(*b*), initial state IS(*b*), complex Fe<sup>II</sup>(*b*); for  $[Fe(CN)_4(L^5)]^{2-}$ , dependences for transition state TS(*c*), initial state IS(*c*), complex Fe<sup>II</sup>(*c*)

in small solvent effects on reactivity; *i.e.* small kinetic solvent effects conceal large solvation changes. The compensation is less clear cut for reaction involving  $[Fe(CN)_2(bipy)_2]$  than for the reactions involving two anions; presumably the differences in products of electric charges are significant. The association constant for  $[Fe(CN)_2(bipy)_2]$  and  $S_2O_8^{2-}$  (sln) will be smaller than that for association of  $[Fe(CN)_4(LL)]^{2-}$  anions with  $S_2O_8^{2-}$  (sln).

The analysis reported here is based essentially on the TATB assumption, leading to ionic transfer chemical potentials. The patterns obtained present a possible challenge to a

 Table 5
 Initial state-transition state analysis of reactivity trends

 for the peroxodisulfate oxidation of iron(II)-cyanide-diimine complexes in DMSO-water mixtures<sup>a</sup>

	vol.% (id) DMSO					
	0	20	40	60		
$[Fe(CN)_{2}(bipy)_{2}]$ $k_{2}$ $\Delta\Delta^{\neq}G$ $\Delta(S_{2}O_{8})^{2-}$ $\Delta(complex)$ $\Delta(is)$ $\Delta(\neq)$	0.33	$0.11 \\ 2.7 \\ 1.8 \\ -2.7 \\ -0.9 \\ 1.8$	0.023 6.6 8.4 - 3.5 4.9 11.5	0.0031 11.5 22 4.3 18 30		
$[Fe(CN)_{4}(bipy)]^{2^{-}}$ $rk$ $\Delta\Delta^{\neq}G$ $\Delta(complex)$ $\Delta(is)$ $\Delta(\neq)$	0.129	0.104 0.5 3.2 5.0 5.5	0.063 1.8 16.2 24.6 26	0.046 2.6 27.9 50 53		
$[Fe(CN)_{4}(L^{5})]^{2} - \frac{k_{2}}{\Delta\Delta^{\neq}G}$ $\Delta(complex)$ $\Delta(is)$ $\Delta(\neq)$	2.1	$12.0 \\ -4.3 \\ 0.1 \\ 1.9 \\ -2.4$	22.5 -5.8 1.1 9.5 4.3	2.5 -0.3 2.0 24 24		

<sup>a</sup> See footnotes to Table 4, except units of  $k_2$  are dm<sup>3</sup> mol<sup>-</sup> s<sup>-1</sup>;  $\Delta(S_2O_8)^{2^-} = \Delta(aq \rightarrow x_2) \ \mu^0(S_2O_8)^{2^-}$ ; sln; concentration scale)/kJ mol<sup>-1</sup>.

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more detailed analysis using the inverse Kirkwood-Buff procedures<sup>24,25</sup> which have been reasonably successfully applied to kinetic data involving neutral solutes.<sup>26</sup>

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# Appendix

# Hexadentate ligands



**Bidentate ligands** 





**Terdentate ligands** 



#### Bridging tetradentate ligand



#### **Encapsulating ligand**



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