Electron Transfer Reactions in Non-aqueous Media. Part I.

Reduction of $CoF(NH_3)_5{}^{2+}$, $CoCl(NH_3)_5{}^{2+}$ and $CoBr(NH_3)_5{}^{2+}$ by Iron(II) in Dimethylsulphoxide

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The kinetics of the reduction of the cobalt(III) octahedral complexes $CoF(NH_3)_5{}^{2+}$, $CoCl(NH_3)_5{}^{2+}$ and $CoBr(NH_3)_5{}^{2+}$, by iron(II) in dimethylsulphoxide (DMSO) have been studied over a range of temperatures, ionic strengths and acidities. As in water the results are consistent with an inner-sphere atom transfer mechanism. An extraordinary change in activation parameters, compared with the aqueous chemistry, for the chloro and bromo systems in DMSO, is interpreted in terms of a change in the stereochemistry of the iron(II) atom in the bridged intermediate.

Introduction

Despite the large amount of work over the last twenty years on electron transfer reactions between metal ions in solution,[1] relatively few papers have reported on the effect of solvent on these reactions.

The most extensively studied exchange reaction in nonaqueous media is that between iron(II) and iron(III). This reaction has been studied in nitromethane[2] and in dimethyl sulphoxide–water,[3,4] isopropanol–water,[5] methanol–water,[6,7] ethanol–water,[7] 1-propanol–water[7] and acetone–water[7] mixtures. Some other exchange reactions in various non-aqueous media have been studied.[1]

Even less work has been done on reactions between different metal ions in non-aqueous solvents. The tetraphenylporphineiron(III) chloride–chromium(II) reaction in benzene was studied[8] and the product criterion applied to prove an inner-sphere mechanism.[1] With iron(II) as reducing agent, however, the primary oxidation product cannot, in general, be identified, since iron(III) is too substitution labile.[9] The iron(II) reductions of *cis*-(N)-[Co(α-ala)$_2$(Ox)]$^-$ and *cis*-(N)-[Co(β-ala)$_2$(Ox)]$^-$ (ala = alanine, Ox = oxalate) have been studied in methanol–water mixtures,[10] and of *cis*-[Co(en)$_2$(NH$_2$CH$_2$CH$_2$OH)Cl]$^{2+}$ in dimethylsulphoxide–water, dimethylformamide–water,

ethanol–water and acetone–water mixtures.[11] No mechanistic interpretations were made.

We chose to study reactions of the type [CoX(NH$_3$)$_5$]$^{2+}$ (where X = F, Cl or Br) with Fe(II) in dimethylsulphoxide and to compare our results with those obtained in water.[12,13] The results in water had only given indirect proof for an inner-sphere mechanism, and it was hoped that by extending the work to a non-aqueous solvent more mechanistic information would be obtained.

Experimental

Materials

[CoCl(NH$_3$)$_5$]Cl$_2$,[14] [CoBr(NH$_3$)$_5$]Br$_2$[15] and [CoF(NH$_3$)$_5$](NO$_3$)$_2$[16] complexes were prepared using previously reported procedures. They were converted to perchlorate salts by standard procedures.[12] [Fe(H$_2$O)$_6$](ClO$_4$)$_2$ was prepared according to the method of Wada and Reynolds.[17] Use of this complex as the source of iron(II) in DMSO leads to water impurities of less than 0.05 mol fraction in the most concentrated solutions and as low as 0.009 mol fraction in the most dilute solutions. The purity of the complexes was checked analytically and spectrophotometrically.

The distillation procedure for the purification of DMSO has been described previously.[18] Potassium perchlorate was recrystallized three times from water. All other chemicals were of the best quality commercially available and were used without further purification.

Kinetic Technique

Care was exercised to exclude oxygen and moisture from the deoxygenated reactant solutions during the mixing procedure and the reaction. Fresh solutions were made up for each days runs.

The reactions were followed spectrophotometrically using a Perkin Elmer 450 spectrophotometer, scanning the entire visible region. The decrease in absorbance

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was followed at the maximum of visible absorption of the cobalt(III) complex. All runs were conducted *in situ* and thermostatted by circulating water through the cell housing from an external thermostat. The temperature was controlled to within 0.1°C and was monitored by means of a copper–constantin thermocouple. A cell of 5 cm path length was used to achieve optimum optical densities at the concentrations chosen.

The chloro and bromo systems were studied under pseudo-first order conditions, with iron(II) in excess. The concentration of cobalt(III) -complex used was 1.35×10^{-3} mol l^{-1} and the iron(II) concentration was varied from 0.02 to 0.11 mol l^{-1}. Pseudo-first order rate constants, k_p, were calculated from the gradient of $\log(D_t–D_\infty)$ *vs.* time data, where D_t and D_∞ are the optical densities at time "t" and after at least ten half lives, respectively. Excellent first order rate plots were obtained for at least three half lives. Second order rate constants, k_2, were calculated using $k_p/[Fe(II)]$.

The fluoro system reacted much faster and for this reason was impossible to study under pseudo-first order conditions. As a result this system was studied under second order conditions with both the iron(II) and cobalt(III) concentrations initially at 1.35×10^{-3} mol l^{-1}. Second order rate constants were obtained from the gradient of a plot of $1/D_t–D_\infty$ *vs.* time, which was linear for at least three half lives.

For all three systems ionic strength was maintained at 0.34 mol l^{-1} with potassium perchlorate or magnesium perchlorate. The substitution of magnesium for potassium had no effect on the rate constants obtained. Acid in the form of toluene-p-sulphonic acid was included at 1.08×10^{-2} mol l^{-1}. Without at least five moles of acid per mole of cobalt(III) complex a side reaction occurred. The NH_3 released after reduction of the cobalt(III) complex coordinates to the iron(III) produced, giving an intense spectrum which interferred with analysis in that it swamped the cobalt(III) spectrum. This added acid converted released NH_3 to NH_4^+ in which form it did not coordinate. Acid could not be included in stock solutions of the fluoro complex as this caused solvolytic loss of fluoride. As a result acid was included in the iron(II) solution for this system. The chloro and bromo complexes did not undergo catalyzed solvolysis in the presence of acid.

Ionic strength dependence, acid dependence and temperature dependence studies were also conducted. The infinity spectra supported the accepted stoichiometry for these reactions: $CoX(NH_3)_5^{2+}$ + Fe $(DMSO)_6^{2+}$ + $5H^+$ → $Co(DMSO)_6^{2+}$ + $5NH_4^+$ + $FeX(DMSO)_5^{2+}$ where X = F, Cl or Br.

Results and Discussion

Kinetic data obey a rate equation first order with respect to both the cobalt(III) complex and iron(II).

$$\frac{-d[Co(III)]}{dt} = k_2[Co(III)][Fe(II)]$$

Table I shows k_p and k_2 for a series of runs at various concentrations of iron(II) for the bromo system. Independence of the calculated values of k_2 upon the concentration of iron(II) confirms second order kinetics. Similar data for the chloro system are presented in Table II. The primary second order data for the fluoro system gave the second order rate constants recorded in Table III. Table III also shows the average value of k_2 obtained at various temperatures for all three systems. The values of k_2 obtained for all systems were at the worst within 4% of the mean value and usually within 3%. It can be seen that the order of reactivity at these temperatures is as in water[12,13] (*i.e.* F>Cl >Br).

For the bromo and fluoro systems, the effect of ionic strength upon the rate, at our fixed acid concentration, was examined. Table IV summarizes the results of this study. A relatively small increase in rate with increasing ionic strength was observed with a non-linear depen-

TABLE I. Rate Constants for the Reaction Fe(II) and [CoBr $(NH_3)_5]^{2+}$ in DMSO.[a]

$[Fe(II)] \times 10^2$ (mol l^{-1})	$k_p \times 10^4 (s^{-1})$	$k_2 \times 10^3 (mol^{-1} l\ s^{-1})$
10.99	2.75	2.50
10.01	2.48	2.48
9.02	2.30	2.55
9.01	2.23	2.48
9.02	2.32	2.57
9.02	2.28	2.53
8.01	1.97	2.46
7.05	1.78	2.52
5.07	1.22	2.40
3.97	0.99	2.49
1.96	0.50	2.55

[a] $[Co(III)Br] = 1.35 \times 10^{-3}$ mol l^{-1}; Temp. $= 25.8°C; \mu = 0.34$ mol l^{-1}; $[H^+] = 1.08 \times 10^{-2}$ mol l^{-1}.

TABLE II. Rate Constants for the Reaction Fe(II) and $[CoCl(NH_3)_5]^{2+}$ in DMSO.[a]

$[Fe(II)] \times 10^2$ (mol l^{-1})	$k_p \times 10^4 (s^{-1})$	$k_2 \times 10^3 (mol^{-1} l\ s^{-1})$
10.05	9.73	9.68
9.01	8.89	9.87
7.98	7.88	9.88
6.01	5.92	9.85
6.02	5.66	9.40
2.01	1.96	9.75

[a] $[Co(III)Cl] = 1.35 \times 10^{-3}$ mol l^{-1}; Temp. $= 25.8°C; \mu = 0.34$ mol l^{-1}; $[H^+] = 1.08 \times 10^{-2}$ mol l^{-1}.

TABLE III. Rate Constants for the Reaction Fe(II) and $[CoX(NH_3)_5]^{2+}$ in DMSO, X = Br, Cl or F.[a]

Oxidizing Agent	Temperature (°C)	k_2(mol^{-1} l s^{-1})
$[CoBr(NH_3)_5]^{2+}$	25.8	2.51×10^{-3}
	29.7	4.27×10^{-3}
	34.2	7.30×10^{-3}
	38.2	11.18×10^{-3}
$[CoCl(NH_3)_5]^{2+}$	25.8	9.72×10^{-3}
	30.3	16.55×10^{-3}
	33.9	27.06×10^{-3}
	38.7	44.28×10^{-3}
$[CoF(NH_3)_5]^{2+}$	21.4	3.68
	25.8	4.73
	29.5	5.67

[a] $[Co(III)X] = 1.35 \times 10^{-3}$ mol l^{-1}; $\mu = 0.34$ mol l^{-1}; [H$^+$] $= 1.08 \times 10^{-2}$ mol l^{-1}.

TABLE IV. Ionic Strength Dependence for the Reaction Fe(II) and $[CoX(NH_3)_5]^{2+}$ in DMSO, X = Br or F.[a]

Oxidizing Agent	k_2(mol^{-1} l s^{-1})	μ(mol l^{-1})
$[CoBr(NH_3)_5]^{2+}$	2.23×10^{-3}	0.29
	2.51×10^{-3}	0.34
	2.74×10^{-3}	0.40
	2.93×10^{-3}	0.46
$[CoF(NH_3)_5]^{2+}$	2.45	0.06
	3.67	0.15
	4.74	0.27
	4.73	0.34
	4.88	0.43

[a] $[Co(III)X] = 1.35 \times 10^{-3}$ mol l^{-1}; [H$^+$] $= 1.08 \times 10^{-2}$ mol l^{-1}; Temp. $= 25.8°$C.

dence of logk_2 *vs.* $\sqrt{\mu}$. The effect of ionic strength on the rate has not been examined in water.

The variation of k_2 with acid concentration was studied for the bromo and fluoro systems, at our fixed

TABLE V. Acid Dependence for the Reaction Fe(II) and $[CoX(NH_3)_5]^{2+}$ in DMSO, X = Br or F.[a]

Oxidizing Agent	k_2(mol^{-1} l s^{-1})	[H$^+$]$\times 10^2$ (mol l^{-1})
$[CoBr(NH_3)_5]^{2+}$	2.36×10^{-3}	0.72
	2.44×10^{-3}	0.82
	2.46×10^{-3}	0.92
	2.55×10^{-3}	1.08
	2.72×10^{-3}	1.41
	2.79×10^{-3}	1.58
	2.72×10^{-3}	1.91
$[CoF(NH_3)_5]^{2+}$	4.70	0.74
	4.91	0.87
	4.73	1.08
	5.00	1.30
	5.61	1.62
	5.61	2.21
	5.66	3.26

[a] $[Co(III)X] = 1.35 \times 10^{-3}$ mol l^{-1}; $\mu = 0.34$ mol l^{-1}; Temp. $= 25.8°$ C.

ionic strength. Table V presents these results. The small effect upon k_2 in both systems of changing acid concentration confirms that there is no large specific hydrogen ion catalysis to associate with the proven catalytic solvolysis in the fluoro system. No acid effect was observed in water.[12,13]

Table VI compares the rate parameters in DMSO with those obtained by Diebler and Taube[12] in water.

As previously indicated indirect proof can be given to justify the assignment of an inner-sphere mechanism for these reactions in water. Some Co(III)X–Fe(II) reactions, where X is a potential bridging group, are sufficiently rapid to enable observation of the formation and decay of the primary iron(III) product, Fe(III)X.[19,20,21] This constitutes direct proof of an inner-sphere mechanism, and all the reactions of this type, for which such a test is possible, have proven to be inner-sphere.

The reactivity order of F > Cl > Br is found for these reactions in water, as it also is with a number of reduc-

TABLE VI. Comparison of Rate Parameters in DMSO and H$_2$O with Fe(II) as Reductant.

Oxidizing Agent	H$_2$O[12]			DMSO		
	k_2[a] mol^{-1} l s^{-1}	ΔH^* kcal mol^{-1}	ΔS^* cal K^{-1} mol^{-1}	k_2 mol^{-1} l s^{-1}	ΔH^* kcal mol^{-1}	ΔS^* cal K^{-1} mol^{-1}
$[CoBr(NH_3)_5]^{2+}$	0.92×10^{-3}	15.6	−20	2.51×10^{-3}	21.7	+2
$[CoCl(NH_3)_5]^{2+}$	1.6×10^{-3}	14.5	−23	9.72×10^{-3}	21.2	+3
$[CoF(NH_3)_5]^{2+}$	7.6×10^{-3}	13.4	−23	4.73	8.8	−26

[a] Temp. $= 25.5°$C; $\mu = 1.7$ mol l^{-1}.

ing agents other than iron(II).[22,23,24] Various workers have rationalized this observation in terms of an inner-sphere mechanism.[12,22] This so called "inverse" order parallels the order of thermodynamic stability for the iron(III) halide complexes. On this basis it was suggested that the "inverse" order is determined by the driving force for reaction and therefore that the inner-sphere mechanism obtains. Haim[25] has compared the stabilities of the transition states rather than the reactivity order and has found the sequence $F > Cl > Br$. This order of transition state stability is the same in the analogous chromium(II) systems, even though chromium(II) displays the "normal" reactivity order, *i.e.* $F < Cl < Br$. Chromium(II) is, of course, a proven inner-sphere reductant.[1] Haim has shown that with proven outer-sphere reductants the transition state stability order is the reverse of that above and as a result suggests that a comparison of stabilities of the transition states, rather than the reactivity order for the series F, Cl, Br and I, could prove a useful indirect criterion for distinguishing between inner- and outer-sphere mechanisms.

Espenson[13] has labelled iron(II) an inner-sphere reductant by comparing the reactivity of iron(II) with the azido and thiocyanato pentaamminecobalt(III) complexes. He suggested an inner-sphere mechanism should show great preference for the symmetrical N_3^- over NCS^-, as found for iron(II) ($k_{N_3^-}/k_{NCS^-} \geq 3 \times 10^3$). Candlin and Halpern[26] confirmed positive values for the volume of activation, consistent with an inner-sphere mechanism.

Thus the available evidence points towards an inner-sphere mechanism for these reactions in water and we feel justified in accepting this to be the case.

Table VI shows that the reactions are faster in DMSO than in water. In water the fluoro system reacts about 5 times faster than the chloro and the chloro about twice as fast as the bromo, while in DMSO the fluoro is about 500 times faster than the chloro and the chloro about 4 times faster than the bromo. These rate differences are clearly not remarkable, however the activation parameters shown in Table VI point to an appreciable change in mechanism for the chloro and bromo systems in DMSO. It is clear that here simple comparisons of rates disguise an important change in mechanism. The first question to be answered is whether this new data is consistent with an inner-sphere mechanism.

Electron transfer in the DMSO systems is less likely to occur by an outer-sphere mechanism than in aqueous solution. In DMSO any outer-sphere activated complex must place the metal centres at a greater distance and also a conductance path through peripheral methyl groups of the coordinated DMSO molecules on the iron(II) is less likely than through coordinated water molecules. Spectral studies[4,11,27] support the conclusion that the reductant species in DMSO

is $Fe(DMSO)_6^{2+}$ and not $Fe(H_2O)_6^{2+}$ or any mixed ligand complex. The Marcus theory for outer-sphere electron transfer[28] predicts an increase in the coulombic repulsion free energy and outer-sphere reorganization free energy for a decrease in the macroscopic dielectric constant, assuming the same ionic species are present in the two solvents. Thus one would expect a transition state for outer-sphere transfer to be less easily available in DMSO than in water. In fact electron transfer in DMSO is faster than in water, where the inner-sphere transition state is established to have a lower free energy than any possible outer-sphere transition state. This rate increase in DMSO could be due solely to the fact that the iron(II) species are different from those found in water or, more likely, the different species are only part of the reason and we do not have an outer-sphere transition state but an inner-sphere one. Due to its inertness the cobalt(III) species will be the same in both solvents and can be ignored for the argument above. Thus we accept that these activation parameters must be rationalized in terms of an inner-sphere mechanism, and further cannot see any reasonable rationalization in terms of an outer-sphere mechanism.

The three aqueous systems and the fluoro system in DMSO form a consistent set with comparable ΔS^* values. The values of the activation parameters in water are quite common for both proven inner-sphere and outer-sphere reactions, however, as previously explained, we accept an inner-sphere mechanism. The lower ΔH^* in DMSO is consistent with a greater loss in solvation energy at the transition state in water, which compensates for the expected greater metal–solvent bond energy in DMSO.[29] The negative entropies of activation derive from the organizational difficulty of achieving a bridged transition state.[30] The transition state for these systems is pictured in Figure 1 and involves a bridged complex with both metals in octahedral centres.

We see the chloro and bromo systems in DMSO as exceptional, both in regard to their high enthalpy and more positive entropy of activation. Figure 2 illustrates our proposed transition state for electron transfer in these two systems. Here, in the bridged complex, the inert cobalt(III) centre remains octahedral but the iron centre is tetrahedral.
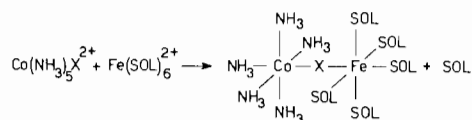
SOL. = DMSO or H_2O

For SOL = DMSO, X = F only; for SOL = H_2O, X = F, Cl and Br.

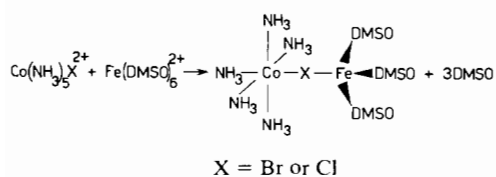Figure 1. Transition state for inner-sphere electron transfer (both metals octahedral).

Co(NH$_3$)$_5$X^{2+} + Fe(DMSO)$_6^{2+}$ → NH$_3$—Co—X—Fe◀DMSO + 3DMSO

X = Br or Cl

Figure 2. Transition state for inner-sphere electron transfer (Co octahedral, Fe tetrahedral).

The substantially more positive value of ΔS^* in these two systems (~ 28 cal K^{-1} mol^{-1} greater than the fluoro system in DMSO) correlates with the release of two additional DMSO molecules in achieving the tetrahedral coordination at iron. Recent work on solvation of simple cations in DMSO[31,32] suggests that the entropy of melting (11.5 cal K^{-1} mol^{-1}) of DMSO is approximately the entropy difference between a bulk DMSO molecule and one in a coordination site. This extra 28 cal K^{-1} mol^{-1} is thus consistent with the release of two extra solvent molecules.

The appreciably greater enthalpy of activation is consistent with the breaking of two extra Fe–DMSO bonds. The value of ΔH^* in these systems is expected to be substantially less than three times the value for the fluoro system ($3 \times 8.8 = 26.4$ kcal mol^{-1}) because inter-ligand repulsive forces are substantially reduced at the tetrahedral centre.

Tetrahedral iron(II) and iron(III) are well documented in the literature.[33,34,35,36] Crystal field stabilization energy favours octahedral over tetrahedral but the difference is· only small, about 3 kcal mol^{-1}. It is significant that although tetrahedral bromo and chloro containing species are found none have been authenticated containing fluoro ligands. All fluoro containing iron complexes appear to be octahedral.

Thus we conclude that an inner-sphere mechanism of electron transfer operates in both DMSO and water.

Preliminary results in DMSO–H$_2$O solvent mixtures point to a sharp discontinuity in activation parameters over a small range in solvent composition for the chloro system, consistent with a change in coordination at the iron centre.

Acknowledgement

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