

Mechanistic Information from the Effects of Pressure on the Kinetics of the Reduction of $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$, $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ by Iron(II) in Dimethylsulphoxide

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The kinetics of reduction of $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$, $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ by $\text{Fe}(\text{II})$ have been studied at 35 °C as a function of pressure up to 1,7 kbar. The volumes of activation were independent of pressure and found to be $+10,3 \pm 0,4$; $+3,8 \pm 0,7$ and $0,0 \pm 0,4 \text{ cm}^3 \text{ mol}^{-1}$ for the three systems, respectively. The results are discussed with reference to earlier work reported in literature. Changes in solvation and possible steric requirements can account for the observed kinetic parameters.

Introduction

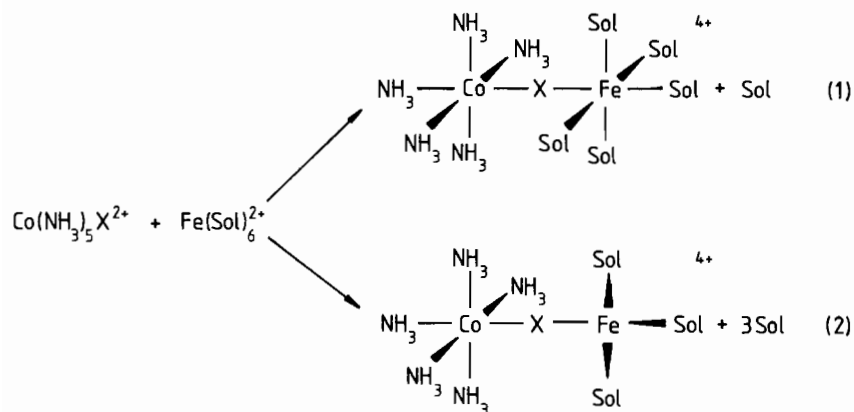
Many electron transfer reactions between metal ions in aqueous solution have been investigated in recent years and the results are well documented [1–3]. In contrast, only a few papers have been published on these reactions in non-aqueous media and the majority of these were devoted to the

exchange reaction between iron(II) and iron(III) [4, 5].

In a recent series of papers, Watts and co-workers [6–8] described the reduction of $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ (where X = F, Cl or Br) by $\text{Fe}(\text{II})$ in dimethylsulphoxide (hereafter referred to as DMSO), in DMSO–water mixtures and in *N,N*-dimethylformamide (hereafter referred to as DMF). They reported significant changes in the second order rate constants and their activation parameters on varying the solvent composition gradually from pure water to pure DMSO. The fluoro, chloro and bromo complexes are believed to react according to an inner-sphere mechanism in DMSO, as is the case in water [6, 7]. The observed changes in activation parameters, which were more marked for the chloro and bromo systems, were interpreted in terms of a change in the stereochemistry of the iron(II) atom from an octahedral to a tetrahedral geometry in the bridged intermediate. For the fluoro system the iron(II) atom was thought to maintain its octahedral coordination throughout the reaction. This concept is presented schematically in Scheme I.

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Scheme I. Reaction (1) for: Sol = DMSO, X = F
 Sol = H₂O, X = F, Cl, Br

Reaction (2) for: Sol = DMSO, X = Cl, Br.

TABLE I. Kinetic Data for the Reduction of $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ by $\text{Fe}(\text{II})$ in DMSO as a Function of Pressure at 35 °C.

X	F	Cl	Br			
$[\text{Co}(\text{NH}_3)_5\text{X}^{2+}], M$	2×10^{-4}	3×10^{-3}	7.5×10^{-3}			
$[\text{Fe}(\text{II})], M$	2×10^{-3}	3×10^{-2}	8.9×10^{-2}			
$[\text{H}^+], M$	6×10^{-3}	2×10^{-2}	4×10^{-2}			
Ionic strength, M	4.7×10^{-1}	4.7×10^{-1}	4.7×10^{-1}			
Pressure bar	k $M^{-1} \text{ sec}^{-1}$		$k \times 10^2$ $M^{-1} \text{ sec}^{-1}$		$k \times 10^2$ $M^{-1} \text{ sec}^{-1}$	
1	12.7	12.8	5.22	4.93	1.42 ^a	1.46
	13.0		5.03	5.14	1.48	1.48
					1.42	1.35 ^b
					1.37	1.52
					1.53	
200	13.4	11.1	5.07	5.02	1.52	1.53
	10.9					
400	11.3	10.1	4.89	4.70	1.54	1.56
	10.5					
600	10.0	9.70	4.59	4.89	1.49	1.58
	10.6	9.06			1.42	1.53
800	8.69	8.17	4.63	4.89	1.56	1.58
	10.3	9.61	4.08	4.36		
1000	9.10	8.46	4.64	4.99	1.58	1.52
	7.77	9.00	4.74	4.15		
1200			4.02	4.28	1.45	1.46
			3.83			
1400			4.38	4.04	1.42	1.43
					1.40	
1700					1.53	1.41

^a $[\text{Fe}(\text{II})] = 0.0488 M$. ^b $[\text{Fe}(\text{II})] = 0.1344 M$.

Watts and co-workers [10] found mixed second order kinetics in DMF and reduction was suggested to proceed via the reversible formation of a halide bridged binuclear intermediate, followed by a rate-determining electron transfer step. The reported activation parameters are once again consistent with a tetrahedral stereochemistry for the iron(II) atom in the bridged intermediate for the chloro and bromo systems, and with an octahedral iron(II) configuration for the fluoro system. The values of the activation parameters reported for the reactions in DMF are in very close agreement with those reported for the corresponding reactions in DMSO.

According to the theoretical predictions made by Stranks [9], the volume of activation ($\Delta V_{\text{exp}}^\ddagger$), calculated from the pressure dependence of the second order rate constant for these types of electron transfer reactions, should be negative when the reaction proceeds via an outer-sphere mechanism. A positive $\Delta V_{\text{exp}}^\ddagger$ is expected for inner-sphere reactions primarily due to the expulsion of a solvent molecule upon forming the bridged intermediate. The validity of these predictions has been illustrated by numerous examples [9]. Halpern [10] reported posi-

tive values for $\Delta V_{\text{exp}}^\ddagger$ for the title reactions in water.

On the basis of the above arguments the activation volumes for the reactions of the chloro and bromo systems in DMSO, in which three solvent molecules are released into the bulk solvent (Scheme I), are expected to be much more positive than that for the other systems for which it is thought that only one solvent molecule leaves the coordination sphere during the formation of the bridged complex. The reaction of the fluoro system in DMSO was originally too fast for conventional high pressure techniques and it has only recently become possible to study this reaction using a special high pressure mixing device [11].

Experimental

The complexes $[\text{Co}(\text{NH}_3)_5\text{F}](\text{ClO}_4)_2$, $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2$ and $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ were prepared according to standard procedures reported in the literature [12–15]. Analyses and spectra were in good agreement with the theoretical values and those published elsewhere [16, 17], respectively. $[\text{Fe}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ was used as a source of iron(II)

TABLE II. Rate and Activation Parameters for the Reduction of $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ by $\text{Fe}(\text{II})$ in H_2O and DMSO .

X		Br	Cl	F	Reference
Solvent		H_2O			
k_{25°	$M^{-1} \text{sec}^{-1}$	0.92×10^{-3}	1.6×10^{-3}	7.6×10^{-3}	15
ΔH^\ddagger	kJ mol^{-1}	65.2	60.6	56.0	
ΔS^\ddagger	$\text{J K}^{-1} \text{mol}^{-1}$	-84	-96	-96	
k_{25°	$M^{-1} \text{sec}^{-1}$	0.73×10^{-3}	1.4×10^{-3}	6.6×10^{-3}	21
ΔH^\ddagger	kJ mol^{-1}	55.6	52.2	57.2	
ΔS^\ddagger	$\text{J K}^{-1} \text{mol}^{-1}$	-117	-125	-96	
k_a	$M^{-1} \text{sec}^{-1}$	1.26×10^{-3} (35°)	1.67×10^{-3} (35°)	3.58×10^{-3} (25°)	10
$\Delta V_{\text{exp}}^\ddagger$	$\text{cm}^3 \text{mol}^{-1}$	+8 (35°)	+8(35°)	+11(25°)	22
$\Delta V_{\text{exp}}^\ddagger$	$\text{cm}^3 \text{mol}^{-1}$	$+6.4 \pm 1.1$ (35°)	$+8.7 \pm 0.3$ (35°)	$+10.7 \pm 0.1$ (25°)	
Solvent		~35 mol % DMSO in H_2O			
k_{26°	$M^{-1} \text{sec}^{-1}$	4.8×10^{-2}	1.23×10^{-1}	4.3	7
ΔH^\ddagger	kJ mol^{-1}	56	48	38	
ΔS^\ddagger	$\text{J K}^{-1} \text{mol}^{-1}$	-81	-102	-105	
Solvent		DMSO (>95 mol %)			
k_{25°	$M^{-1} \text{sec}^{-1}$	2.51×10^{-3}	9.72×10^{-3}	4.73	6
ΔH^\ddagger	kJ mol^{-1}	90.7	88.6	36.8	
ΔS^\ddagger	$\text{J K}^{-1} \text{mol}^{-1}$	+8	+12	-108	
k_{35°	$M^{-1} \text{sec}^{-1}$	1.49×10^{-2}	5.13×10^{-2}	12.9	This work
$\Delta V_{\text{exp}}^\ddagger$	$\text{cm}^3 \text{mol}^{-1}$	0.0 ± 0.4 (35°)	$+3.8 \pm 0.7$ (35°)	$+10.3 \pm 0.4$ (35°)	This work

^aTemperature indicated in brackets.

and was prepared according to the method of Wada and Reynolds [18]. It was stored under a nitrogen atmosphere and standardized from time to time with potassium permanganate. By using this complex in DMSO a water content of between 0.1 and 5 mol% was introduced [6, 7]. Acid was added to the reaction solutions in the form of *p*-toluene-sulphonic acid (recrystallized from methanol) to inhibit any side reactions [6] between iron(III) and NH_3 released during the reduction of the $\text{Co}(\text{III})$ complexes. The acid concentration was at least five times the $\text{Co}(\text{III})$ complex concentration. The ionic strength of these solutions was adjusted with potassium perchlorate. DMSO was purified according to a standard distillation procedure [19].

All reactions were followed spectrophotometrically using a Zeiss DMR 10 spectrophotometer at 330 nm (fluoro system), 550 nm (chloro system) and 560 nm, (bromo system). The chloro and bromo systems were studied in a conventional thermostatted ($\pm 0.05^\circ\text{C}$) high pressure cell [20]. Due to the higher reactivity of the fluoro system, a rapid mixing modification [11] was built into the existing high pressure cell. Pseudo first order conditions were maintained for each system and the observed first order rate constants, k_{obs} , were calculated from the slopes of $\ln(A_t - A_\infty)$ versus time plots, where A_t and A_∞

are the absorbances at time *t* and at infinity, respectively. Excellent first order plots were obtained for at least three to four half-lives.

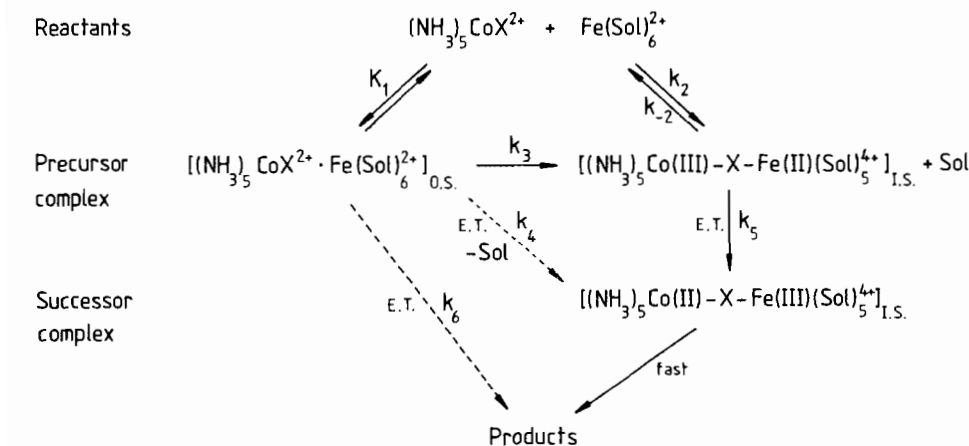
Results and Discussion

For the kinetic data in DMSO at normal pressure, k_{obs} depends linearly on $[\text{Fe}(\text{II})]$ such that $k_{\text{obs}} = k[\text{Fe}(\text{II})]$, in agreement with that reported by Matthews and Watts [6, 7]. The values of the second order rate constant, *k*, are given in Table I as a function of pressure up to 1,7 kbar. Plots of $\ln k$ versus *p* are linear, within experimental error, for all three systems and the activation volume, $\Delta V_{\text{exp}}^\ddagger$, was estimated in the usual way. No attempt was made to correct the observed $\Delta V_{\text{exp}}^\ddagger$ values for the compressibility of the solvent. The rate constants and activation parameters for the reactions in DMSO , together with those in H_2O , are summarized in Table II.

The reactivity order $\text{F} > \text{Cl} > \text{Br}$ observed in H_2O [10], also holds for $\text{DMSO-H}_2\text{O}$ mixtures [7] and pure DMSO [6]. In the latter, the fluoro system becomes extremely reactive and the reactivity order may be presented as $\text{F} \gg \text{Cl} > \text{Br}$. Changes in solvent are accompanied by significant changes in the activation parameters, ΔH^\ddagger and ΔS^\ddagger , as mentioned previously [6, 7], and in the activation volumes now

reported. On the basis of the suggested mechanism [6, 7] outlined in the introductory section (Scheme I), more positive $\Delta V_{\text{exp}}^\ddagger$ values are expected for the reduction of the chloro and bromo complexes in DMSO than for both the fluoro complex in DMSO and all three complexes in H_2O . However, the $\Delta V_{\text{exp}}^\ddagger$ values in Table II reflect the opposite tendency and are therefore not in accord with the suggestions made by Watts *et al.* [6, 7]. Thus we have attempted to find alternative ways to interpret the observed experimental results.

Redox reactions of the type investigated are relatively complicated in that precursor complex formation, intramolecular electron transfer and/or successor complex decomposition may be rate-determining [23]. Therefore the observed values of k , ΔH^\ddagger , ΔS^\ddagger and $\Delta V_{\text{exp}}^\ddagger$ may comprise contributions made by one or more of the mentioned reaction steps, thus complicating the interpretation of such data. A general reaction scheme, which includes all possible pathways, is presented in Scheme II.



Scheme II. Sol = solvent molecule, H_2O or DMSO
 X = halide atom, Cl, Br or F
 O.S. = outer-sphere complex
 I.S. = inner-sphere complex
 E.T. = electron transfer reaction.

It is generally accepted [10, 15, 21], and we underline this concept, that the reduction of $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}$) by $\text{Fe}(\text{II})$ in H_2O proceeds via an inner-sphere mechanism in which the electron transfer step is rate-determining. Since $\text{Fe}(\text{II})$ is extremely labile in H_2O , substitution cannot be rate-determining [23]. As the formation of the inner-sphere complex is substitution controlled, and since the plots of k_{obs} versus $[\text{Fe}(\text{II})]$ are not curved and do not reach a limiting value at high $[\text{Fe}(\text{II})]$, it may be concluded that $K_2 (= k_2/k_{-2})$ is relatively small, especially when compared to that found in DMF [8]. Thus only a small percentage of the reactant species is present in the form of an inner-sphere precursor complex. The literature values for ΔS^\ddagger

comply with highly ordered transition states, similar in structure to the inner-sphere precursors.

Within the concept of electron transfer being rate-determining, the reported [10] $\Delta V_{\text{exp}}^\ddagger$ values are attributable to volume changes incurred during precursor formation and the actual activation volumes for electron transfer, *i.e.* $\Delta V_{\text{exp}}^\ddagger = \Delta \bar{V}_{\text{PC}} + \Delta V_{\text{ET}}^\ddagger$ (see Scheme II). $\Delta V_{\text{ET}}^\ddagger$ is expected to be small and independent of X, based on preliminary results on the pressure dependence of the spectra of mixed valence complexes [24]. $\Delta \bar{V}_{\text{PC}}$ on the other hand will consist of three major contributions. Firstly, a large volume increase due to the release of a solvent molecule on forming the inner-sphere precursor complex [9, 10]. Secondly, a small negative contribution resulting from changes in electrostriction on forming a 4+ species from two 2+ charged ions. It is perhaps more significant that both contributions are also independent of the nature of X. Nevertheless, the $\Delta V_{\text{exp}}^\ddagger$ values [10] are positive and do increase with decreasing size of the potential bridging halide atom

X (see the recalculated [26] values quoted in Table II). Thus the third contribution to $\Delta \bar{V}_{\text{PC}}$, stemming from bond formation between $\text{Fe}(\text{II})$ and X, must be negative, which is in agreement with the basic concepts involved in high pressure studies [25]. Furthermore, the magnitude of this contribution will depend on the size of both species involved in bond formation and vary with the Van der Waals radii of the various X atoms ($\text{F} \ 1.35 \text{ \AA}$, $\text{Cl} \ 1.80 \text{ \AA}$, $\text{Br} \ 1.95 \text{ \AA}$) [26].

On increasing the DMSO content of the solvent [7], the second order rate constants increase and reach maximum values at approx. 35 mol% DMSO. Up to this point the activation parameters (see Table II) show a decrease in ΔH^\ddagger , whereas ΔS^\ddagger is approx. constant when compared to pure H_2O as solvent. Furthermore, it is important to note that this effect decreases in the order $\text{F} > \text{Cl} > \text{Br}$. To account for these observations we suggest that mainly solvation changes around the reactant, precursor and transition state species are responsible for these effects.

The decrease in solvation energy can be expected to be most dramatic for the $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ reactants, particularly for the fluoro complex. A comparison of the partial molar volumes of these ions in water ($\text{Co}(\text{NH}_3)_5\text{F}^{2+}$, 57.9 ± 0.5 ; $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$, 85.8 ± 0.4 ; $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$, $95.1 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$; cf. the individual ions: F^- , 3.3; Cl^- , 21.7; Br^- , 29.4 $\text{cm}^3 \text{ mol}^{-1}$ [28] shows that water undergoes exceptionally strong electrostriction in the presence of the fluoro complex ion. This may be partially attributed to strong hydrogen bonding between the solvent and the very basic fluoride ligand. The presence of an aprotic solvent, such as DMSO, will tend to disrupt such interactions thereby increasing the reactivity of the fluoride ligand towards the Fe(II) center, resulting in an increase in K_2 .

This is in general agreement with the predictions [7] made from criteria of Amis [29], but contrary to the hypothesis of Watts *et al.* [7]. Displacement of the aquo ligands on Fe(II) by DMSO will, according to these predictions, only become significant at higher DMSO concentrations (*i.e.* >35 mol%). Also, a weakening of the precursor-solvent interaction requires that less energy be spent in rearranging the solvation shell of the precursor prior to electron transfer, thereby enhancing this step (presented by k_5 in Scheme II).

The possibility cannot be ruled out, that in the presence of DMSO the diffusion controlled formation of the outer-sphere complex (step K_1) may also contribute to the formation of the inner-sphere species via k_3 . In other words K_1k_3 may become larger than K_2 under such conditions. In addition, the reactivity order observed emphasizes the importance of solvational changes and is reflected in the decrease in ΔH^\ddagger . The virtually constant value of ΔS^\ddagger is not surprising as no change in mechanism is proposed (*i.e.* k_5 remains rate-determining), regardless of the relative magnitudes of K_2 and K_1k_3 . Formation of the precursor complex is associated with a loss of motional entropy [4] and obviously principally accounts for the negative ΔS^\ddagger values found here.

The large increase in rate constant for the fluoro system on going from H_2O to 35 mol % DMSO is not necessarily extraordinary. For instance the rate constant for the reduction of $\text{Co}(\text{NH}_3)_5\text{SCN}^{2+}$ by Fe(II) is approx. 10^5 times larger at 25 °C than for the reduction of $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ [30]. Both reactions are nevertheless thought to proceed via inner-sphere mechanisms in which electron transfer is rate-determining. The difference is ascribed to the effect of the bridging ligand. In almost pure DMSO the fluoro system behaves identically to that in 35 mol% DMSO. Substitution of the aquo ligands on Fe(II) by DMSO does not seem to affect either the formation of the inner-sphere complex or the electron transfer within the fluoro system. The activation

volume for the reduction of this system in almost pure DMSO (Table II) is in very good agreement with the reported value for pure H_2O , and can be considered as a strong indication that the same mechanism holds in both solvents.

Alternative possibilities do exist for the fluoro system in DMSO, with outer-sphere formation taking place and leading either directly to products via k_6 or to the successor complex via k_4 with the simultaneous release of a DMSO molecule. The k_6 path can be rejected on the basis of calculations [9] mentioned in the introduction, where strongly negative $\Delta V_{\text{exp}}^\ddagger$ values are predicted. However, the k_4 path will result in a positive $\Delta V_{\text{exp}}^\ddagger$ value due to the effect of the leaving solvent molecule on forming the successor complex. Reactions with k , ΔH^\ddagger and ΔS^\ddagger values very similar to those found for the fluoro system in DMSO have been regarded as "probably outer-sphere" in the literature [31]. Therefore we cannot completely rule out the possibility that the mechanism for the reduction of $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ in DMSO may have some outer-sphere character.

ΔH^\ddagger and ΔS^\ddagger for the reduction of the chloro and bromo complexes increase markedly on increasing the DMSO content of the solvent from 35 to almost 100 mol% [7, 32]. Such changes in activation parameters have previously [23, 33] been considered as evidence for substitution, represented by k_2 and/or k_3 in Scheme II, becoming rate-determining in similar redox reactions. There exists some evidence from mixed-solvent studies that substitution reactions involving Fe(II) are associative in character [34, 35]. Molecular models show that the formation of a seven coordinated Fe(II) transition state would involve considerable steric crowding especially for the larger "bridging groups" such as Cl^- and Br^- . Naively this would explain the decrease in the observed rate constants for the reaction of the chloro and bromo systems with increasing DMSO content of the solvent. It is also in keeping with the smaller positive values for $\Delta V_{\text{exp}}^\ddagger$ found for these two systems due to reduced stretching of the Fe-DMSO bond. It is known [36] that the application of pressure tends to increase the rate of associative type reactions which involve steric crowding at the reaction center. However, strongly negative ΔS^\ddagger values would be anticipated, more negative in fact than observed in the 0-35 mol% DMSO region. The small positive values found for these reactions would then suggest that the substitution process is rather of the I_a type.

A very recent solvent exchange study [37] of Fe(II) in DMSO (actually a mixture of DMSO- d_3 nitromethane) and DMF has shown, contrary to previous work, that the rate of exchange in these two solvents is very fast ($>10^6 \text{ sec}^{-1}$ at 25 °C) and, very significantly, virtually equal to the water exchange rate. Notwithstanding the difficulties encountered in obtaining reliable solvent exchange

data [37], these results seem to establish that the electron exchange reactions studied in this work are unlikely to be substitution controlled in DMSO. The ΔH^\ddagger , ΔS^\ddagger and $\Delta V_{\text{exp}}^\ddagger$ values, which were determined as overall parameters for the entire process, would still include significant contributions from the substitution processes involved.

From the kinetic studies in DMSO/H₂O mixtures it would appear that the replacement of coordinated water molecules on the Fe(II) ion is a gradual process with respect to increasing the DMSO content of the solvent and becomes kinetically observable at ca. 35 mol% DMSO. The introduction of DMSO molecules into the first coordination sphere of Fe(II) leads to an increase in steric crowding around the metal. The effect of this steric hindrance could be twofold. Firstly, for larger bridging groups the formation constant for the precursor complex, whether designated by K_2 or K_1k_3 , will be reduced in magnitude. Secondly, steric crowding of the bridging group may influence the Fe(II)-X bond length, increasing it with increasing size of X, thereby reducing the efficiency of the rate-determining electron transfer process, k_5 . Both effects depend on the size of X and one must therefore assume that fluoride is sufficiently small as to not encounter any significant steric hindrance, so that the rate constant, ΔH^\ddagger and ΔS^\ddagger remain constant in DMSO/H₂O mixtures over the range, ca. 35 mol % DMSO to almost pure DMSO. However, it is apparent that the chloride and bromide ligands do suffer from the effects of steric crowding as demonstrated by the decrease in rate constant, originating from the marked increase in ΔH^\ddagger above 35 mol% DMSO. As mentioned earlier, the application of pressure tends to "aid" reactions in overcoming steric hindrance [36]. The values for $\Delta V_{\text{exp}}^\ddagger$ for the chloro and bromo systems are approx. 5 cm³ mol⁻¹ more negative in DMSO than in H₂O and may be readily accounted for by a pressure enhancement of K_2 . Certainly in organic chemistry such effects are well documented and may be in excess of 20 cm³ mol⁻¹ [36]. It is important to note that the moderate pressures employed here will have no detectable effect on the Co-X-Fe bond lengths or angles and will therefore not influence the electron transfer step, i.e. $\Delta V_{\text{ET}}^\ddagger$ [38]. As already mentioned for the analogous reactions in water, the absolute values of $\Delta V_{\text{exp}}^\ddagger$ in DMSO are most certainly dictated by the large positive contribution due to the release of a DMSO molecule upon forming the precursor complex. However, this contribution, as well as that due to changes in the overall extent of electrostriction upon forming the 4+ charged precursor, should be independent of the nature of X and thus a constant factor in each system. These contributions will be compensated to varying degrees, depending on the Van der Waals radii of the bridging ligand, by a negative intrinsic contribution due to Fe(II)-X bond formation.

To sum up, we conclude that the observed changes in k , ΔH^\ddagger , ΔS^\ddagger and $\Delta V_{\text{exp}}^\ddagger$ for the reduction of $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ (X = F, Cl, Br) by Fe(II) in DMSO may be explained in terms of the same mechanism as was found in H₂O, namely an inner-sphere, electron transfer rate-determining process. Variations in these parameters are then due to changes in solvation and the introduction of steric crowding rather than changes in the coordination number of Fe(II), as suggested earlier [6, 7]. These conclusions illustrate the usefulness of $\Delta V_{\text{exp}}^\ddagger$ values as a strong discriminating parameter for distinguishing between possible mechanisms of complicated reactions.

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