MECHANISTIC INFORMATION FROM THE EFFECT OF PRESSURE ON SOME TYPICAL OUTER-SPHERE ELECTRON-TRANSFER REACTIONS OF Co(III) COMPLEXES

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The effect of pressure on a number of outer-sphere electron-transfer reactions was studied using conventional and stopped-flow kinetic techniques. The investigated systems are:

$$Co(NH_3)_5 X^{(3-n)+} + Fe(CN)_6^{4-} \rightarrow Co^{2+} + 5NH_3 + X^{n-} + Fe(CN)_6^{3-}$$
(1)

 $(X = H_2O, py, Me_2SO and Cl^-),$

 $Co(terpy)_{2}^{2+} + Co(bpy)_{3}^{3+} \rightarrow Co(terpy)_{2}^{3+} + Co(bpy)_{3}^{2+}$ (2)

Reaction (1) was studied in water, whereas reaction (2) was studied in water, formamide and acetonitrile. Reaction (1) proceeds via the formation of an ion-pair precursor, followed by the electron-transfer step. The volumes of activation for the electron transfer step are large positive quantities (between 27 and $34 \text{ cm}^3 \text{ mol}^{-1}$) and can largely be accounted for on the basis of solvational changes on the iron center. Reaction (2) does not involve the formation of ion-pairs, and the volumes of activation for the electron-transfer step vary between -5 and $-14 \text{ cm}^3 \text{ mol}^{-1}$ depending on the solvent employed. Partial molar volume measurements enable the construction of a reaction volume profile, which assists the mechanistic interpretation of these data. A comparison with theoretically expected volumes of activation is given and deviations are discussed.

1. Introduction

The effect of pressure on a few inner-sphere electron-transfer reactions was investigated in earlier studies performed in our laboratories [1– 3]. The complexity of these systems, however, did not allow a detailed interpretation of the observed pressure effects. Outer-sphere electrontransfer reactions are, on the other hand, significantly simpler since they do not involve bond formation between the redox partners. Stranks [4] developed an equation, based on the principles of the Hush-Marcus theories, to account for the effect of pressure on outer-sphere electrontransfer reactions. The apparent agreement between the theoretically predicted and experimentally observed volumes of activation, $\Delta V^{\#}$, is presumably one of the reasons why such measurements were not pursued. However, it was recently shown [5] that Strank's theoretically predicted values are in error and that his equation cannot account for the observed ΔV^{*} data [5,6]. We

have therefore undertaken a systematic study of the effects of pressure on various outer-sphere electron-transfer reactions [7, 8], as outlined by reactions (1) and (2) in the Abstract.

2. Reduction of $Co(NH_3)_5 X^{(3-n)+}$ by $Fe(CN)_6^{4-}$

Outer-sphere electron-transfer in this system proceeds via the formation of ion pairs, and can be expressed as in reactions (3) and (4). Under pseudo-first-order conditions, i.e. excess

$$\operatorname{Co}(\mathrm{NH}_{3})_{5} \mathrm{X}^{(3-n)^{+}} + \operatorname{Fe}(\mathrm{CN})_{6}^{4^{-}}$$

$$\stackrel{\kappa}{\longleftrightarrow} \left\{ \operatorname{Co}(\mathrm{NH}_{3})_{5} \mathrm{X}^{(3-n)^{+}} \cdot \operatorname{Fe}(\mathrm{CN})_{6}^{4^{-}} \right\}, \qquad (3)$$

$$\{ \text{Co}(\text{NH}_3)_5 X^{(3-n)^+} \cdot \text{Fe}(\text{CN})_6^{4^-} \}$$

$$\xrightarrow{k_{\text{ET}}} \text{Co}^{2^+} + 5\text{NH}_3 + X^{n^-} + \text{Fe}(\text{CN})_6^{3^-}, \qquad (4)$$

Fe(II), the observed rate constant can be

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expressed as in (5), from which it follows that plots of k_{obs} versus [Fe(II)]

$$k_{\rm obs} = k_{\rm ET} K[{\rm Fe(II)}] / \{1 + K[{\rm Fe(II)}]\}$$
(5)

should be curved and reach a limiting value at high [Fe(II)]. A typical example of such plots for the reduction of $Co(NH_3)_5Me_2SO^{3+}$, as a function of pressure, is given in fig. 1. Values for the ion-pair formation constant (K) and electrontransfer rate constant (k_{ET}) can be obtained from plots of k_{obs}^{-1} versus [Fe(II)]⁻¹ [9]. From the temperature and pressure dependencies of K and k_{ET} , the thermodynamic and kinetic parameters, summarized in table I, were estimated in the usual way. Typical semilogarithmic plots of k_{ET} versus pressure are given in fig. 2.

The data in table I clearly demonstrate that reaction (4) is characterized by a large positive value for $\Delta V^{\#}$, which is accompanied by a fluctuating positive value for ΔS^{*} . The data also show that ion-pair formation exhibits almost no change, or a slight decrease, in molar volume. The more positive value in the case of the chloro complex is in line with the tendency that intrinsic volume changes during ion-pair formation will depend on the charge on the cobalt species. The volume of activation for the electron transfer reaction (4) is independent of the nature of X^{n-} , indicating that changes in volume on the cobalt center do not influence ΔV^* significantly. This is in contrast to the arguments presented by Saito et al. [10] and calls for a detailed analysis.



Fig. 1. Effect of pressure on k_{obs} as a function of [Fe(II)] for the reduction of Co(NH₃)₅Me₂SO³⁺ by Fe(CN)₆⁴⁻ at 25°C and ionic strength 1 M.



Fig. 2. Effect of pressure on $k_{\rm ET}$ for the reaction of $Co(NH_3)_5 X^{3+}$ by $Fe(CN)_6^{4-}$ in aqueous medium.

Table I Rate and activation parameters for the system

$Co(NH_3)_5 X^{(3-n)+}$	+ Fe(CN) ₆ ⁴⁻ $\stackrel{K}{\longleftrightarrow}$ {Co(NH ₃) ₅ X ⁽³⁻ⁿ⁾⁺ · Fe(CN) ₆ ⁴⁻ }
	$\downarrow k_{\rm ET}$
	$Co^{2+} + 5NH_3 + X^{n-} + Fe(CN)_6^{3-}$

X ^{<i>n</i>-}	K at 25°C (M ⁻¹)	$\Delta ar{V}$ (°C) (cm ³ mol ⁻¹)	k _{ET} at 25℃ (s ⁻¹)	ΔH^{*} (kJ mol ⁻¹)	$\frac{\Delta S^{*}}{(J K^{-1} mol^{-1})}$	$\frac{\Delta V^*}{(\text{cm}^3 \text{ mol}^{-1})}$
H,O	480 ± 110	-15 ± 8	$(10.0 \pm 0.2) \times 10^{-2}$	89 ± 3	38 ± 8	26.5 ± 2.4 (25)
py	168 ± 7	а	$(8.9 \pm 0.3) \times 10^{-3}$	118 ± 8	113 ± 29	29.8 ± 1.3 (15)
Me ₂ SO	34 ± 4	-11 ± 3	$(2.0 \pm 0.1) \times 10^{-1}$	84 ± 2	25 ± 8	34.4 ± 1.1 (25)
CI	36 ± 2	+2 ± 1	$(2.8 \pm 0.3) \times 10^{-2}$	77 ± 9	14 ± 32	26.1 ± 1.3 (35)

^a Not determined.

Electron transfer within the reactant ion-pair results in the formation of a product ion-pair consisting of $Co(NH_3)_5 X^{(2-n)+}$ and $Fe(CN)_6^{3-}$. Recent partial molar volume measurements and theoretical predictions [8, 10] indicate that a volume increase of about $20 \text{ cm}^3 \text{ mol}^{-1}$ is expected when Co(III) is reduced to Co(II). On the other hand, partial molar volume data for the iron species indicate that $Fe(CN)_{4}^{3-}$ is about 43 cm³ mol⁻¹ larger than $Fe(CN)_{6}^{4-}$ [11]. It follows that the increase in volume during such an electron-transfer step is mainly due to volume changes on the Fe center within the ion pair. In this way it is understandable why ΔV^{*} is fairly independent of the nature of X^{n-} . In addition, the quoted partial molar volume differences indicate that the transition state is approximately half-way along the reaction coordinate, on a volume basis, during the electron transfer step.

3. Reduction of $Co(bpy)_3^{3+}$ by $Co(terpy)_2^{2+}$

The electron-transfer reaction outlined in (2) (bpy = 2,2'-bipyridine, terpy = 2,2',6',6"-terpyridine) is not expected to involve significant ion-pairing due to the similarity in charge on the participating species. Under pseudo-first-order conditions, i.e. excess Co(III), $k_{obs} = k[Co(III)]$, where k represents the second-order rate constant for the electron-transfer reaction. The temperature [12] and pressure (fig. 3) dependencies of k were measured in various solvents and the corresponding activation parameters are summarized in table II. It follows that electron transfer is accom-



Fig. 3. In k versus pressure for the reduction of $Co(bpy)_3^{3+}$ by $Co(terpy)_2^{2+}$ in three solvents (S) at 25°C and ionic strength 0.01 M.

panied by negative values for ΔS^{*} and ΔV^{*} in all solvents.

The theoretical treatment developed by Stranks [4] should be applicable to such simple electron-transfer processes. According to this treatment $\Delta V^{\#}$ can be expressed in terms of contributions from coulombic interaction, solvent rearrangement, internal rearrangement and a Debye-Hueckel component, as indicated in eq. (6). Applications of the expressions for these

$$\Delta V^{\#} = \Delta V_{\text{coul}}^{\#} + \Delta V_{\text{SR}}^{\#} + \Delta V_{\text{IR}}^{\#} + \Delta V_{\text{DH}}^{\#}$$
(6)

terms [4] and taking Wherland's correction [5] into account, result in the following contributions towards $\Delta V^{\#}$, namely -4.8, -3.9, ~0 and +1.4 cm³ mol⁻¹, respectively [8]. It follows, that the theoretically expected $\Delta V^{\#}$ for the electron-transfer reaction in water is -7.3 cm³ mol⁻¹,

$\operatorname{Co}(\operatorname{terpy})_2^{2^+} + \operatorname{Co}(\operatorname{bpy})_3^{3^+} \xrightarrow{k} \operatorname{Co}(\operatorname{terpy})_2^{3^+} + \operatorname{Co}(\operatorname{bpy})_3^{2^+}$								
Solvent	$k \text{ at } 25^{\circ}\text{C}^{a}$ (M ⁻¹ s ⁻¹)	$\frac{\Delta H^{\# b}}{(\text{kJ mol}^{-1})}$	$\frac{\Delta S^{\# b}}{(J K^{-1} mol^{-1})}$	ΔV^* at 25°C ^a (cm ³ mol ⁻¹)				
H,O	26.2	21	-155	-9.4 ± 0.9				
HCONH,	9.1	51	-50	-13.8 ± 1.1				
CH ₃ CN	1.3	29	-146	-5.1 ± 1.4				

Table II Rate and activation parameters for the reaction

^a Data determined in this study, ionic strength = 0.01 M.

^b Data taken from ref. 12, ionic strength = 0.0027 - 0.0046 M.

which is remarkably close to the experimentally observed value of (-9.4 ± 0.9) cm³ mol⁻¹. Similar calculations for the reaction in the other solvents is more complicated and preliminary results [8] indicate larger discrepancies between the theoretically predicted and experimentally observed data. Nevertheless, the theoretical treatment developed by Stranks [4] does present a realistic description for this outer-sphere electron-transfer reaction in water as solvent. We are presently continuing this work to resolve discrepancies referred to before [5, 6].

Acknowledgements

The authors gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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