Volumes of Activation for Outer-sphere Electron Transfer between Cobalt-(II) and -(III) in Solution

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The volume of activation for outer-sphere electron transfer between $Co(terpy)_2^{2+}$ and $Co(bpy)_3^{3+}$ (terpy = 2,2′,6′,2″-terpyridine, bpy = 2,2′-bipyridine) in dilute aqueous solution (−9 ± 1 cm³ mol⁻¹ at 25 °C and ionic strength 0.01 M) is close to that predicted by the conventional Hush–Marcus theories.

Stranks[1] developed an equation, based on the principles of the Hush–Marcus theories, to account for the effect of pressure on outer-sphere electron transfer reactions. His apparently close correlation between predicted and experimentally observed volumes of activation was recently pointed out[2] to be wrong due to an error in the sign of the Debye–Hückel component $\Delta V^{\ddagger}_{DH}$ in the overall expression (1), where $\Delta V^{\ddagger}_{coul}$, $\Delta V^{\ddagger}_{SR}$, and $\Delta V^{\ddagger}_{IR}$ represent the contributions from coulombic interaction, solvent rearrangement, and internal rearrangement of the complex ions, respectively.[1] For example, Stranks[1] measured a value of -19.8 ± 1.5 cm^3 mol^{-1} at 65 °C for the outer-sphere self-exchange of $Co(en)_3^{2+/3+}$ (en = ethylenediamine), which is in very close agreement with his estimated value of -18.4 cm^3 mol^{-1}. However, Wherland[2] pointed out that the latter value should be -7.5 cm^3 mol^{-1}, *i.e.* significantly more positive than the experimentally obtained value. The apparent agreement shown by Stranks[1] is presumably one of the reasons why such measurements were not pursued for simple outer-sphere electron transfer systems.

$$\Delta V^{\ddagger} = \Delta V^{\ddagger}_{coul} + \Delta V^{\ddagger}_{SR} + \Delta V^{\ddagger}_{IR} + \Delta V^{\ddagger}_{DH} \qquad (1)$$

Recently, Swaddle *et al.*[3] measured $\Delta V^{\ddagger}$ for electron transfer between MnO_4^- and MnO_4^{2-} in aqueous alkaline solution and found a value (-21 ± 1 cm^3 mol^{-1} at 45 °C and ionic strength 1.1 M) significantly more negative than can be accounted for by the corrected Stranks theory, *viz.* -6 cm^3 mol^{-1}. We have in the meantime investigated the effect of pressure on the outer-sphere electron transfer reaction between $Co(terpy)_2^{2+}$ and $Co(bpy)_3^{3+}$ [4] (terpy = 2,2′,6′,2″-terpyridine, bpy = 2,2′-bipyridine), and found a volume of activation for the reaction in aqueous solution which is very close to that predicted by the corrected Stranks theory.

Farina *et al.*[5] measured rate and activation parameters for the $Co(terpy)_2^{2+}$–$Co(bpy)_3^{3+}$ system in fifteen different solvents at ambient pressure, and reported a reasonably good correlation between the redox rate constants and the differences in the reciprocals of the dielectric constants of the solvents relative to water. Our density measurements in water[4] indicated that the partial molar volumes of the cationic terpy and bpy complexes are very similar for a particular oxidation state of cobalt and approximately 10 cm^3 mol^{-1} larger for Co^{II} than for Co^{III}. It follows that the overall reaction volume for the electron transfer process is close to zero, and no significant intrinsic volume effects are expected to contribute towards $\Delta V^{\ddagger}$. In addition, we do not expect significant ion-pair formation or large solvational changes to complicate the interpretation of $\Delta V^{\ddagger}$ since the reactant and product species are closely related cations. Other outer-sphere electron transfer reactions, involving the reduction of Co^{III} complexes by $Fe(CN)_6^{4-}$, have been shown to be significantly more complicated than the present system due to these inherent effects.[6–8]

The redox reaction between $Co(terpy)_2^{2+}$ and $Co(bpy)_3^{3+}$ was studied under pseudo-first-order conditions in water, formamide, and acetonitrile as a function of pressure using conventional[9] and stopped-flow[10] kinetic techniques. Figure 1 shows that ln k (k is the second-order rate constant) is a linear function of pressure. The corresponding volumes of activation are summarized along with the other available activation parameters in Table 1. The activation parameters for the reaction in water and acetonitrile are very similar, but differ significantly from those for the reaction in formamide. In the latter case $\Delta H^{\ddagger}$ is significantly higher, whereas $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ are significantly different. These differences cannot be accounted for by the small difference in ionic strength, and must be related to the ability of the solvent to stabilize the transition state of greater charge than either reactant. The negative values of $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ also indicate that solvational changes during the electron transfer process must present a

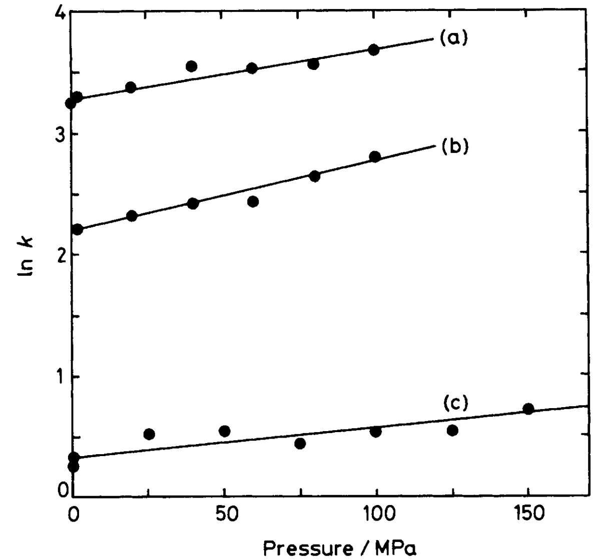

Figure 1. Plot of ln *k* *vs.* pressure for the reduction of $Co(bpy)_3{}^{3+}$ by $Co(terpy)_2{}^{2+}$ in three solvents (a) H_2O, (b) $HCONH_2$, and (c) MeCN at 25 °C and ionic strength 0.01 M.

major contribution. Since it is not appropriate to discuss such kinetic data in any further detail here, we will only concentrate on a comparison of the $\Delta V^{\ddagger}$ for the reaction in water with that predicted by the corrected Stranks theory.[1,2]

Our calculation[4] of the terms in equation (1) using the expressions given elsewhere,[1,2] results in $\Delta V^{\ddagger}_{coul} = -4.8$, $\Delta V^{\ddagger}_{SR} = -3.9$, and $\Delta V^{\ddagger}_{DH} = +1.4$ cm^3 mol^{-1}. We can safely assume that $\Delta V^{\ddagger}_{IR} \sim 0$ [1,3,4] such that $\Delta V^{\ddagger} = -7.3$ cm^3 mol^{-1} at 25 °C and ionic strength 0.01 M. It is important to note that the Debye–Hückel contribution depends on the selected value for the distance of closest approach, which we calculated to be 1.05 nm from the partial molar volume data.[4] Stranks selected a value of 0.81 nm for the closely related ethylenediamine system,[1] which would increase $\Delta V^{\ddagger}_{DH}$ slightly to +1.5 cm^3 mol^{-1}. However, for the present system the Debye–Hückel component is small and hardly contributes towards the overall $\Delta V^{\ddagger}$. Furthermore, our calculated $\Delta V^{\ddagger}$ value is very close to that estimated by Wherland[2] for the ethylenediamine system, *viz.* -7.5 cm^3 mol^{-1}. It follows that the theoretically predicted value for $\Delta V^{\ddagger}$ is in close agreement with that found experimentally for the $Co(terpy)_2{}^{2+}$–$Co(bpy)_3{}^{3+}$ system in water. A possible reason for the deviation in the case of Stranks' and Swaddle's systems[1—3] may be found in medium effects at high ionic strengths, *i.e.* beyond the Debye–Hückel range. A theoretical prediction of $\Delta V^{\ddagger}$ for the redox reaction in the other solvents is more complicated, and our preliminary results[4] indicate significant differences. Nevertheless, it is encouraging to conclude that this simple theoretical approach[1,2] does present a realistic $\Delta V^{\ddagger}$ value for an outer-sphere redox reaction in dilute aqueous solution.

Table 1. Activation parameters for the reaction[a,b] $Co(terpy)_2{}^{2+} + Co(bpy)_3{}^{3+} \rightarrow Co(terpy)_2{}^{3+} + Co(bpy)_3{}^{2+}$.

Solvent	$\Delta H^{\ddagger}$ /kJ mol^{-1}	$\Delta S^{\ddagger}$ /J K^{-1} mol^{-1}	$\Delta V^{\ddagger}$ (25 °C) /cm^3 mol^{-1}
H_2O	21	−155	−9.4 ± 0.9
$HCONH_2$	51	−50	−13.8 ± 1.1
MeCN	29	−146	−5.1 ± 1.4

[a] $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ data were taken from ref. 5. The ionic strength for water and acetonitrile was 0.0027 M, and for formamide 0.0046 M. [b] $\Delta V^{\ddagger}$ data were determined in this study[4] for which an ionic strength of 0.01 M was selected.

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