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Concerning the Pressure Dependence of Outer-Sphere Electron-Transfer Reactions: the Reduction of $Co(NH_3)_5OH_2^{3+}$ by $Fe(CN)_6^{4-}$ in Aqueous Acidic Solution

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The reduction of $Co(NH_3)_5OH_2^{3+}$ *was studied as a function of* $[Fe(CN)_6^{4-}]$ *for pressures up to 1000 bar at 25 °C using a high-pressure stopped-flow instrument. The ion-pair formation and electron-transfer rate constants were estimated as a function of pressure using a double reciprocal plot treatment of the rate data. The corresponding reaction volume and volume of activation were found to be −15.5 and +26.4* cm^3 mol^{-1} *respectively. These results are discussed in reference to earlier reported data for some typical outer-sphere electron transfer reactions.*

Introduction

Recent reports [1–3] have reviewed the processes involved in outer-sphere electron-transfer reactions. The complex nature of such processes has encouraged us to apply high pressure techniques to the investigation of such systems in an effort to gain better insight into the intimate mechanisms involved in such processes. Our earlier studies [4–6] in the area of inner-sphere redox reactions revealed some surprising results, which further stimulated our interests.

Stranks [7] reported the first information on the effect of pressure on some typical outer-sphere electron-transfer reactions. From his theoretical treatment he predicted significantly negative volumes of activation for the Fe(III)/Fe(II) and Co(III)/Co(II) redox reactions. Major contributions from coulombic interaction, solvent rearrangement and hydrogen bonding effects were suggested to account for these values. The validity of his theoretical predictions [7] was underlined by some closely-corresponding, experimentally-determined volumes of activation. Ion-pairing or encounter complex formation did not play a significant role in any of the studied systems, since they all involved electron-transfer reactions between positively charged species.

Very recently, Saito and co-workers [8] reported results for the effect of pressure on the outer-sphere electron-transfer reaction within the ion-pair between $[Mo(V)_2O_4(edta)]^{2-}$ and $[(NH_3)_5Co(III)\text{-}(\mu\text{-}O_2^-)\text{-}Co(III)(NH_3)_5]^{5+}$. They found an overall volume change upon activation of 36 cm^3 mol^{-1}, which is indeed a very significant pressure effect and differs markedly from that reported by Stranks [7] for electron-transfer between similarly charged species.

The reduction of $Co(NH_3)_5OH_2^{3+}$ by $Fe(CN)_6^{4-}$ at normal pressure was studied in detail by Gaswick and Haim [9]. An outer-sphere redox mechanism, which included the formation of an ion-pair intermediate, was suggested to account for the reported kinetic results.

$$\begin{array}{l}Co(NH_3)_5OH_2^{3+} + Fe(CN)_6^{4-} \overset{K}{\rightleftharpoons} \\ \qquad \{Co(NH_3)_5OH_2^{3+}\cdot Fe(CN)_6^{4-}\} \\ \qquad\qquad \downarrow k \\ \qquad Co^{2+} + 5NH_3 + Fe(CN)_6^{3-} + H_2O\end{array} \tag{1}$$

The corresponding pseudo-first-order rate constant is given by

$$k_{obs} = kK[Fe(CN)_6^{4-}]/\{1 + K[Fe(CN)_6^{4-}]\} \tag{2}$$

from which k and K can be estimated by measuring k_{obs} as a function of $[Fe(CN)_6^{4-}]$, and following the double reciprocal plot treatment [9].

Experimental

$[Co(NH_3)_5OH_2](ClO_4)_3$ was prepared as described elsewhere [10, 11]. UV-visible spectra were in good agreement with those reported before [10]. The

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TABLE I. k_{obs} as a Function of [$Fe(CN)_6^{4-}$] and Pressure for the Reduction of $Co(NH_3)_5OH_2^{3+}$ in Aqueous Solution.[a]

[$Fe(CN)_6^{4-}$] × 10^3 *M*	$k_{obs}{}^b \times 10^2$, sec^{-1}				
	P (= bar) = 25	250	500	750	1000
3	6.97 ± 0.47	5.31 ± 0.19	4.45 ± 0.16	3.81 ± 0.14	3.08 ± 0.33
4	7.24 ± 0.78	5.67 ± 0.26	4.81 ± 0.09	3.83 ± 0.14	2.79 ± 0.08
6	7.51 ± 0.82	6.55 ± 0.23	5.27 ± 0.19	3.82 ± 0.24	3.43 ± 0.09
10	9.31 ± 0.19	8.27 ± 0.31	6.26 ± 0.22	4.47 ± 0.27	3.43 ± 0.09
20	10.74 ± 0.17	9.49 ± 0.70	6.69 ± 0.27	5.32 ± 0.28	3.94 ± 0.22
30	10.77 ± 0.34	9.19 ± 0.28	6.49 ± 0.19	5.13 ± 0.08	4.42 ± 0.15

[a] [Co(III)] = 5 × 10^{-4} *M*; [H_2EDTA^{2-}] = 1 × 10^{-3} *M*; [CH_3COOH] = [CH_3COO^-] = 2.5 × 10^{-2} *M*; pH = 4.7; Temp. = 25 °C; ionic strength = 0.5 *M*; wavelength = 420 nm. [b] Mean value of between 6 and 18 kinetic runs.

TABLE II. Values of k and K as a Function of Pressure.

Pressure bar	Estimated from[a] plots of k_{obs}^{-1} *versus* [Fe(II)]$^{-1}$		Estimated from[a,b] plots of k_{calc}^{-1} *versus* [Fe(II)]$^{-1}$	
	k × 10^2 sec^{-1}	K M^{-1}	k × 10^2 sec^{-1}	K M^{-1}
25	11.2 ± 0.7	483 ± 112	11.9 ± 0.7	393 ± 72
250	10.4 ± 0.5	324 ± 45	9.4 ± 0.5	446 ± 76
500	7.1 ± 0.2	538 ± 60	7.1 ± 0.3	519 ± 92
750	5.2 ± 0.3	737 ± 246	5.4 ± 0.3	611 ± 129
1000	4.2 ± 0.3	684 ± 256	4.2 ± 0.2	731 ± 201
Volume quantities, cm^3 mol^{-1}	+26.5 ± 2.4[c]	−15.4 ± 7.9[d]	+26.4 ± 0.1[c]	−15.5 ± 0.4[d]

[a] See Discussion; for conditions see Table I. [b] k_{calc} was estimated as outlined in the Discussion. [c] $\Delta\bar{V}^{\neq}$. [d] $\Delta\bar{V}$.

redox reaction was studied under conditions similar to those adopted by Gaswick and Haim [9] in which acetic acid/sodium acetate is used to buffer the system and H_2edta^{2-} is added to complex the produced Co^{2+}. The ionic strength of the test solutions was adjusted with $NaClO_4$. Doubly-distilled water and chemicals of analytical reagent grade were used throughout the investigation.

The redox reaction was studied using a thermostatted (±0.1 °C) high-pressure stopped-flow system [12], in which one syringe contained the Co(III)/H_2edta^{2-}/acetate buffer solution and the other syringe the $Fe(CN)_6^{4-}/NaClO_4$ solution. k_{obs} was calculated in the usual way, and the corresponding first-order plots were linear for at least three half-lives of the reaction. No concentration corrections for the compressibility of the solvent were made, since this only amounts to 3% at 1000 bar.

Results and Discussion

k_{obs} was measured as a function of [$Fe(CN)_6^{4-}$] at various pressures and the results are summarized in Table I. Under some conditions, experimental error limits as high as 10% were observed and up to 18 kinetic runs were performed to obtain representative mean values*. Plots of k_{obs} versus [$Fe(CN)_6^{4-}$] are indeed strongly curved as expected, and the results were treated according to the double reciprocal plot proceudre, *i.e.* k_{obs}^{-1} *versus* [Fe-

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*The order of magnitude of the measured rate constants is actually too small to justify kinetic measurements on a stopped-flow instrument under normal conditions. However, this is the only possible way to follow such reactions at elevated pressures, and can as such partially account for the error limits found under such conditions.

$(CN)_6^{4-}]^{-1}$. The values of k and K, obtained in this manner, are summarized in Table II. The values of K are subjected to large errors since they are estimated from a combination of the intercepts and slopes of the inverse plots. An alternative treatment of the data [13], in which ln k_{obs} is plotted *versus* pressure at each $[Fe(CN)_6^{4-}]$, and values of k_{obs} are calculated from the best fit lines and treated in the way outlined above, results in more accurate values of k and especially K as shown in Table II. Plots of lnk and lnK *versus* pressure are linear within the experimental error limits and the values of $\Delta\bar{V}^{\neq}(k)$ and $\Delta\bar{V}(K)$ are included in Table II. Although very similar results are obtained using the two data treatment procedures, it follows that the experimental error limits are significantly reduced in the second procedure.

Haim *et al.* [9] reported values for k and K of $(1.9 \pm 0.1) \times 10^{-1}$ sec^{-1} and $1000 \pm 100\, M^{-1}$, respectively, at 25 °C, $[H_2edta^{2-}] = 1 \times 10^{-3}$ *M*, ionic strength = 0.1 *M* and ambient pressure. These values are in fair agreement with the values reported at 25 bar in Table II, especially if the difference in ionic strength (0.5 compared to 0.1 *M*) is taken into consideration*. The negative value of $\Delta\bar{V}(K)$ strongly differs from the positive value, *viz.* 23.7 ± 3.0 cm^3 mol^{-1}, reported by Saito *et al.* [8] for the formation of the ion-pair between $[Mo(V)_2O_4(edta)]^{2-}$ and $[(NH_3)_5Co(III)\text{-}(\mu\text{-}O_2^-)\text{-}Co(III)(NH_3)_5]^{5+}$. In the latter case the large volume increase was ascribed to changes in the solvation sphere accompanied by the formation of an ion-pair with a +3 charge from two separated ions with charges of −2 and +5. This is presumably not the case in the present system, since charge neutralization would result in a positive value for $\Delta\bar{V}(K)$ [8, 16]. Presumably the charges of the two components of the ion-pair are significantly separated to prevent such charge neutralization. However, we cannot offer a reasonable explanation for the surprisingly negative value of $\Delta\bar{V}(K)$ at this stage, and hope that further studies will resolve the apparent discrepancy.

The large positive volume of activation for the electron-transfer step, *i.e.* $\Delta\bar{V}^{\neq}(k)$, illustrates that significant bond breakage and/or charge neutralization occur during this reaction. Saito *et al.* [8] found a value of +12.1 ± 1.9 cm^3 mol^{-1} for the corresponding reaction in their system, and suggested that the sign of $\Delta\bar{V}^{\neq}$ was due to the change in dipole moment of the precursor complex on going to the transition state. Both these values differ significantly from the value of −13.6 ± 0.8 cm^3 mol^{-1}, which we recently reported [5] for the inner-sphere electron-transfer reaction between *cis*-$Co(en)_2Cl_2^+$ and Fe(II) in DMSO. Furthermore, the nature of the outer-sphere electron-transfer mechanism is such that it is highly unlikely that atom transfer will contribute to the value of $\Delta\bar{V}^{\neq}(k)$. The decomposition of the Co(II) product in reaction (1) is generally assumed to occur rapidly following the electron-transfer step, and as such should not influence the value of $\Delta\bar{V}^{\neq}(k)$. We therefore conclude that the neutralization of charges during the electron-transfer reaction, *i.e.* from a 3+/4− to a 2+/3− species, must largely account for the value of +26.4 cm^3 mol^{-1} obtained for $\Delta\bar{V}^{\neq}(k)$. A similar effect can account for the value of +12.1 cm^3 mol^{-1} reported by Saito *et al.* [8]. In the latter case the effect may be significantly smaller since the main charge component, *viz.* +5, is delocalized over a large binuclear bridged Co(III) species.

Finally, a comparison of the present findings with those reported by Stranks [7] reveals an interesting difference: his electron-transfer reactions between positively charged reactants gave negative volumes of activation of between −13 and −20 cm^3 mol^{-1}. Such processes do not involve any net change in charge, and the earlier mentioned components (see Introduction) must account for these negative values. Furthermore, these values seem to correspond very closely with that found for $\Delta\bar{V}(K)$, *i.e.* the formation of the precursor ion-pair species, in this study. On the other hand, the positive volumes of activation for electron-transfer between oppositely charged species (ref. 8 and this work), can only be ascribed to charge neutralization effects.

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References

1 R. D. Cannon, Inorganic Reaction Mechanisms, Vol. 5, A. McAuley (Ed.), Chemical Society Special Periodical Reports, Chapter 1 (1977).

2 D. E. Pennington, Coordination Chemistry, Vol. 2, A. E. Martell (Ed.), ACS Monograph 174, 476 (1978).

3 R. D. Cannon, Electron Transfer Reactions, Butterworths (1980).

4 R. van Eldik, D. A. Palmer and H. Kelm, *Inorg. Chim. Acta, 29,* 253 (1978).

5 R. van Eldik and H. Kelm, *Inorg. Chim. Acta, 60,* 177 (1982).

6 R. van Eldik, *Inorg. Chem., 21,* 2501 (1982).

7 D. R. Stranks, *Pure Appl. Chem., 38,* 303 (1974).

8 Y. Sasaki, F. B. Ueno and K. Saito, *J. Chem. Soc. Chem. Comm.,* 1135 (1981).

9 D. Gaswick and A. Haim, *J. Am. Chem. Soc., 93,* 7347 (1971).

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*It is generally known that ion-pair formation constants decrease with increasing ionic strength [14, 15].

10 R. van Eldik and G. M. Harris, *Inorg. Chem.*, *19*, 880 (1980).
11 F. Basolo and R. K. Murmann, *Inorg. Synth.*, *4*, 172 (1953).
12 R. van Eldik, D. A. Palmer, R. Schmidt and H. Kelm, *Inorg. Chim. Acta*, *50*, 131 (1981).
13 R. van Eldik, D. A. Palmer and H. Kelm, *Inorg. Chem.*, *18*, 572 (1979).
14 M. J. Pavelich, S. M. Maxey and R. C. Pfaff, *Inorg. Chem.*, *17*, 564 (1978).
15 R. van Eldik, D. A. Palmer and H. Kelm, *Inorg. Chem.*, *18*, 1520 (1979).
16 Typical values of $\Delta\bar{V}$ for ion-pair formation have been summarized by T. Asano and W. J. le Noble, *Chem. Rev.*, *78*, 407 (1978).