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Concerning the Pressure Dependence of Inner-Sphere Electron-Transfer Reactions: the Reduction of *Cis*-$Co(en)_2Cl_2^+$ by Iron(II) in Dimethylsulphoxide

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The title reaction was studied as a function of iron(II) concentration for pressures up to 1250 bar at 30 °C. A double reciprocal plot treatment enabled the estimation of the inner-sphere precursor formation constant and the electron-transfer rate constant as functions of pressure. The corresponding reaction volume and volume of activation were found to be +15.6 ± 0.9 and −13.6 ± 0.8 cm³ mol⁻¹, respectively. These results are discussed in reference to an earlier suggested mechanism and relevant volume data reported in the literature.

Introduction

In general, inner-sphere electron-transfer reactions for complexes of the type $Co(NH_3)_5X^{2+}$ (X = Cl, Br, F, N_3, *etc.*) with Fe(II) occur according to the mechanism [1–9]

$$Co(NH_3)_5X^{2+} + Fe(Sol)_6^{2+} \overset{K}{\rightleftharpoons} [(NH_3)_5Co{-}X{-}Fe(Sol)_5]^{4+} + Sol \xrightarrow{k} Co^{2+} + Fe(Sol)_5X^{2+} + 5NH_4^+ \quad (1)$$

where Sol = solvent, K = inner-sphere precursor formation constant and k = electron-transfer rate constant. The pseudo-first-order rate constant (k_{obs}), determined at excess [Fe(II)], is given by

$$k_{obs} = \frac{kK[Fe(II)]}{1 + K[Fe(II)]} \quad (2)$$

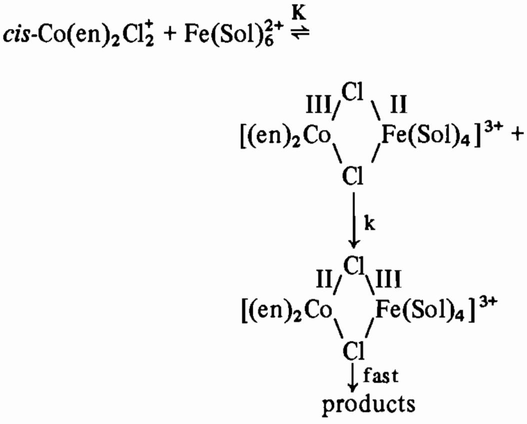
which usually simplifies to

$$k_{obs} = kK[Fe(II)] \quad (3)$$

since K is very small for Sol = H_2O, DMSO and 1 + K[Fe(II)] ~ 1 for most of the studied systems [10, 11]. The effect of pressure on such redox processes results in an observed volume of activation that represents contributions from both [8, 9] the equilibration and the rate-determining steps according to $\Delta\bar{V}^{\neq}_{exp} = \Delta\bar{V}(K) + \Delta\bar{V}^{\neq}(k)$. In none of the investigated systems could these terms be separated, which seriously complicated the interpretation of $\Delta\bar{V}^{\neq}_{exp}$. Furthermore, it was assumed that the magnitude of $\Delta\bar{V}^{\neq}_{exp}$ is governed by contributions from $\Delta\bar{V}(K)$.

Stranks [12] estimated that outer-sphere electron-transfer processes exhibit strongly negative values for $\Delta\bar{V}^{\neq}_{exp}$, mainly due to contributions from coulombic interactions, solvent rearrangement and interionic interactions during the processes. His estimated values [12] are indeed very close to those observed experimentally for some typical outer sphere redox reactions. In addition, Stranks extended his arguments to systems in which electron transfer proceeds according to an inner-sphere mechanism as indicated in reaction (1). The large difference in $\Delta\bar{V}^{\neq}_{exp}$ for inner- and outer-sphere redox reactions was ascribed [12] to the effect of the release of a solvent molecule during the formation of the precursor complex. However, no direct measurement or estimation of $\Delta\bar{V}^{\neq}(k)$ was made.

Recently Watts *et al.* [13] reported kinetic data for the reduction of *cis*-$Co(en)_2Cl_2^+$ by Fe(II) in DMSO, and suggested the following inner-sphere redox mechanism



$$cis\text{-}Co(en)_2Cl_2^+ + Fe(Sol)_6^{2+} \overset{K}{\rightleftharpoons} [(en)_2\overset{III}{Co}(\mu\text{-}Cl)_2\overset{II}{Fe}(Sol)_4]^{3+} + 2Sol \xrightarrow{k} [(en)_2\overset{II}{Co}(\mu\text{-}Cl)_2\overset{III}{Fe}(Sol)_4]^{3+} \xrightarrow{fast} \text{products} \quad (4)$$

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TABLE I. k_{obs} as a Function of [Fe(II)] and Pressure for the Reduction of *cis*-$Co(en)_2Cl_2^+$ by Fe(II) in DMSO.[a]

p = 10 bar		p = 500 bar		p = 1000 bar		p = 1250 bar	
$[Fe(II)]^b \times 10^2$ M	$k_{obs} \times 10^3$ sec^{-1}	$[Fe(II)]^b \times 10^2$ *M*	$k_{obs} \times 10^3$ sec^{-1}	$[Fe(II)]^b \times 10^2$ *M*	$k_{obs} \times 10^3$ sec^{-1}	$[Fe(II)]^b \times 10^2$ *M*	$k_{obs} \times 10^3$ sec^{-1}
2.51	1.17	2.60	1.16	2.53	1.22	2.49	1.03
2.52	1.19	2.46	1.12	2.51	1.20	2.55	1.15
2.94	1.43	2.86	1.30	2.93	1.30	2.89	1.32
2.96	1.45	2.88	1.38	2.92	1.30	2.92	1.28
3.34	1.50	3.27	1.57	3.30	1.50	3.34	1.53
3.31	1.62	3.35	1.51	3.29	1.49	3.31	1.47
4.03	1.73	3.37	1.57	3.98	1.83	4.01	1.73
4.01	1.74	4.02	1.78	4.01	1.73	4.01	1.79
4.97	2.22	4.03	1.84	3.99	1.71	4.96	2.11
5.00	2.29	4.96	2.20	4.96	2.36	5.01	2.02
6.67	2.89	4.97	2.25	4.99	2.16	6.62	2.71
6.66	2.80	6.67	2.75	4.96	2.26	6.62	2.78
		6.66	2.71	6.67	2.95		
				6.60	2.70		

[a] $[Co(III)] = 2.5 \times 10^{-3}$ *M*, $[H^+] = 1.8 \times 10^{-2}$ *M*, ionic strength = 0.35 *M*, temp. = 30 °C, wavelength = 530 nm. [b] Weighed as $[Fe(OH_2)_6](ClO_4)_2$.

TABLE II. Data Obtained from Plots[a] of k_{obs}^{-1} *versus* $[Fe(II)]^{-1}$.

Pressure bar	Intercept (k^{-1}) sec	Slope $(kK)^{-1}$ *M* sec	$k \times 10^2$ sec^{-1}	K M^{-1}	$kK \times 10^2$ M^{-1} sec^{-1}
10	62 ± 23	19.4 ± 0.8	1.6 ± 0.6	3.2 ± 1.2	5.1 ± 0.2
500	45 ± 19	20.4 ± 0.7	2.2 ± 0.9	2.2 ± 0.9	4.9 ± 0.2
1000	35 ± 25	20.7 ± 0.9	2.8 ± 2.0	1.7 ± 1.2	4.8 ± 0.2
1250	31 ± 26	21.8 ± 0.9	3.2 ± 2.7	1.4 ± 1.2	4.6 ± 0.2
Volume quantities, cm^3 mol^{-1}			-13.6 ± 0.8^b	$+15.6 \pm 0.9^c$	$+2.0 \pm 0.5^d$

[a] Using the data recorded in Table I. [b] $\Delta\bar{V}^{\neq}$. [c] $\Delta\bar{V}$. [d] $\Delta\bar{V}^{\neq}_{exp}$.

A similar suggestion was made for this redox reaction in water [14]. The magnitude of K is such that plots of k_{obs} *versus* [Fe(II)] are curved [13], from which the magnitude of K and k could be estimated employing the double reciprocal plot treatment. The pressure dependence of this reaction has now been studied in an effort to determine $\Delta\bar{V}(K)$ and $\Delta\bar{V}^{\neq}(k)$ from the pressure dependences of K and k, respectively.

Experimental Section

cis-$[Co(en)_2Cl_2]ClO_4$ and $[Fe(OH_2)_6](ClO_4)_2$ were prepared as described in the literature [13, 15, 16]. U.V.–visible spectra of the cobalt complex are in good agreement with those reported elsewhere [14, 17, 18]. *p*-toluene sulphonic acid and $KClO_4$ were used to control the acidity and ionic strength of the test solutions respectively. Freshly distilled DMSO and chemicals of analytical reagent grade were used in all solutions. Kinetic measurements were performed on a modified Zeiss PMQ II spectrophotometer equipped with a thermostatted high pressure cell [19], under conditions almost identical to those adopted by Watts *et al.* [13]. k_{obs} was calculated in the usual way, and the corresponding first-order plots were linear for at least three to four half-lives of the reaction. The [Fe(II)] was not corrected for the compressibility of the solvent, since this only amounts to a 3% modification at 1000 bar.

Results and Discussion

Preliminary measurements indicated that under the experimental conditions employed, the solvolysis of *cis*-$Co(en)_2Cl_2^+$ in the absence of Fe(II) in

TABLE III. Data Obtained from Plots[a] of $k_{obs}/[Fe(II)]$ *versus* k_{obs}.

Pressure bar	Intercept k K × 10^2 M^{-1} sec^{-1}	Slope K M^{-1}	Intercept/Slope k × 10^2, sec^{-1}
10	5.1 ± 0.2	2.7 ± 1.0	1.9 ± 0.7
500	5.0 ± 0.1	2.9 ± 0.8	1.7 ± 0.5
1000	4.8 ± 0.2	1.5 ± 1.0	3.1 ± 1.9
1250	4.6 ± 0.2	1.8 ± 0.9	2.5 ± 1.2
Volume quantities cm^3 mol^{-1}	+1.7 ± 0.3[b]	+10.9 ± 5.6[c]	−9.2 ± 5.5[d]

[a] Using the data recorded in Table I. [b] $\Delta\bar{V}^{\neq}_{exp}$. [c] $\Delta\bar{V}$. [d] $\Delta\bar{V}^{\neq}$.

DMSO is too slow to compete with the electron-transfer process [13]. This contrasts the findings for the reaction in water, for which a significant contribution of the aquation reaction was observed during the redox process [14, 18, 20].

The values of k_{obs} are summarized in Table I as a function of [Fe(II)] and pressure. Although k_{obs} increases markedly with increasing [Fe(II)], no distinct pressure dependence can be observed at first sight. The plots of k_{obs} *versus* [Fe(II)] exhibit slight curvature and the data were fitted according to the double reciprocal method using a least-squares analysis. The results in Table II indicate that the intercepts of such plots are relatively small and are subject to considerable errors. This is understandable if one considers the magnitude of k_{obs}^{-1} which varies between ~350 and ~950 sec at each pressure. On the other hand, the slopes of these plots can be determined more accurately and the overall correlation coefficient was at least 0.98 in each case. For this reason the values of k and K in Table II exhibit large error limits, since their estimations involve the values of the intercept. Surprisingly however, plots of ln k, ln K and ln kK *versus* pressure are linear with a relatively strong confidence, such that the corresponding volume data (Table II) exhibit small error limits.

In order to see whether these effects are real, an alternative treatment of the data was used. Equation (2) can be rewritten as

$$\frac{k_{obs}}{[Fe(II)]} = -K\, k_{obs} + kK \qquad (5)$$

such that plots of $k_{obs}/[Fe(II)]$ *versus* k_{obs} should be linear with intercepts = kK and slopes = −K. The data in Table I were plotted in this manner, and the results obtained using a least-squares programme are summarized in Table III. With this procedure more accurate intercepts (*i.e.* kK) and less accurate slopes are obtained. The correlation coefficients for these plots were very low (between 0.4 and 0.7), and significantly larger deviations are observed in the pressure dependences of K and k. However the overall observed tendencies and magnitudes for the volume quantities are very similar to those reported in Table II. We therefore conclude that the observed effects must be real, and prefer the first data processing procedure since significantly better correlation coefficients and more accurate volume data were obtained.

The value of kK in Table II at 10 bar and 30 °C is very close to the value (5.23 ± 0.03) × 10^{-2} M^{-1} sec^{-1} reported by Watts *et al.* [13] at 32 °C and ambient pressure. The small positive value of $\Delta\bar{V}^{\neq}$ (kK) is of the same order of magnitude as the values reported [8, 9] for the reduction of $Co(NH_3)_5X^{2+}$ (X = Cl, Br, N_3) by Fe(II) in DMSO. In addition, we can now conclude that this results from a combination of a large positive value for $\Delta\bar{V}$(K) and a negative value for $\Delta\bar{V}^{\neq}$(k). During the formation of the bridged precursor species the volume decrease due to bond formation is overcompensated by the volume increase resulting from the release of DMSO. The net positive value of $\Delta\bar{V}$(K) illustrates the large effect of the release of DMSO molecules, but does not provide a definite prediction of the number of bridging atoms, *i.e.* number of released DMSO molecules.

A very interesting piece of information is the negative volume of activation for the electron-transfer step. It is of the same order of magnitude as the values reported by Stranks [12] for some typical outer-sphere electron-transfer reactions, during which no bonds are formed or broken. The actual meaning of this value is rather uncertain at this stage since no such values have been previously reported for inner-sphere redox reactions. The results could be an indication that atom transfer plays a significant role during the electron-transfer step, since this could be accompanied by charge delocalisation and a subsequent volume decrease. It is hoped that the situation can be clarified by investigations of typical outer-sphere redox reactions treated in the same manner as presented here, *i.e.* the separation of the precursor-formation step from the electron-transfer process.

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