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Outer-Sphere electron-transfer and the effect of linkage isomerism in the titanium(III) reduction of nitro-pentacyanocobaltate(III) and nitro-, and nitrito-pentaamminecobalt(III) complexes in aqueous acidic media

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Abstract

The reductions of $[\text{Co}(\text{CN})_5\text{NO}_2]^{3-}$, $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$ and $[\text{Co}(\text{NH}_3)_5\text{ONO}]^{2+}$, by Ti^{III} in aqueous acidic solution have been studied spectrophotometrically. Kinetic studies were carried out using conventional techniques at an ionic strength of 1.0 mol dm^{-3} (LiCl/HCl) at $25.0 \pm 0.1^\circ\text{C}$ and acid concentrations between 0.015 and $0.100 \text{ mol dm}^{-3}$. The second-order rate constant is inverse—acid dependent and is described by the limiting rate law: $k_2 \approx k_0 + k[\text{H}^+]^{-1}$, where $k = k'K_a$ and K_a is the hydrolytic equilibrium constant for $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$. Values of k_0 obtained for $[\text{Co}(\text{CN})_5\text{NO}_2]^{3-}$, $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$ and $[\text{Co}(\text{NH}_3)_5\text{ONO}]^{2+}$ are $(1.31 \pm 0.05) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $(4.53 \pm 0.08) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $(1.7 \pm 0.08) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ respectively, while the corresponding k' values from reductions by TiOH^{2+} are $10.27 \pm 0.45 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $14.99 \pm 0.70 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $17.93 \pm 0.78 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ respectively. Values of K_a obtained for the three complexes lie in the range $(1-2) \times 10^{-3} \text{ mol dm}^{-3}$ which suggest an outer-sphere mechanism.

Introduction

Titanium(III) reductions of several metal complexes have been studied [1–2]. Its reductions of the cationic cobalt(III) complexes $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ ($\text{X} = \text{Cl}^-$, Br^- , SO_4^{2-}) have been shown to proceed by an outer-sphere mechanism, but the equivalent reaction for the fluoro complex proceeds by an inner-sphere mechanism [2]. Mechanistic studies on titanium(III) reduction of the cobalt(III) complexes, $[\text{Co}(\text{CN})_5\text{X}]^{2+}$ ($\text{X} = \text{F}^-$, Cl^- , Br^-) were reported by Ojo *et al.* [1] to proceed by outer-sphere mechanism.

The linkage isomerization of NO_2^- bound to metal ammine complexes has been extensively studied and reviewed by various workers [3–8]. Base-catalyzed nitrito to nitro linkage isomerism in cobalt(III) complexes has been reported in the literature [9]. However, to the best of our knowledge, the effect of linkage isomerism in the titanium(III) reductions of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$ and $[\text{Co}(\text{NH}_3)_5\text{ONO}]^{2+}$ in acid medium have not been reported in the literature. This present study investigates the importance of coulombic effects in the $\text{Ti}^{\text{III}}/[\text{Co}(\text{CN})_5\text{NO}_2]^{3-}$ reaction relative to its cationic pentaammine cobalt(III) analogues $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$ and $[\text{Co}(\text{NH}_3)_5\text{ONO}]^{2+}$, and the effects of linkage isomerism in the titanium(III) reductions of these complexes.

Experimental

Materials

$\text{K}_3[\text{Co}(\text{CN})_5\text{NO}_2]$ was prepared by the reaction of $\text{K}_3[\text{Co}(\text{CN})_5\text{N}_3]$ with KNO_2 as described in the literature [10]. The purity of the complex was checked from its IR and uv-visible spectra. IR analysis gave sharp bands at 2133 cm^{-1} , 1380 cm^{-1} and 853 cm^{-1} which are in agreement with earlier results [10]. The electronic spectrum showed a sharp peak at $\lambda_{\text{max}} 300 \text{ nm}$ ($\epsilon = 1077 \text{ M}^{-1} \text{ cm}^{-1}$). $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ was synthesized according to the method of Weston [11] and characterized by its Electronic and IR spectra. The results agreed well with the literature values [11]. $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ was prepared using the method of Willand and Hall [12]. The salmon pink $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ was characterized by running its IR and electronic spectra. The results were in good agreement with the literature [12].

$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ solution was prepared from Ti metal according to the literature procedure [13–15], and standardized by Oyetunji *et al.* by both titrimetric [16] and spectrophotometric methods. The results agreed within 5%. The free acid concentration in the Ti^{III} solution was determined as described by [16] and Ojo *et al.* [1]. Analar grade LiCl and May and Baker grade HCl (36%, density 1.18 g/cm^3) were used to prepare standardized solutions for maintaining ionic strength.

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Kinetics

All the reactions were monitored using a Pye–Unicam SP6/500 uv spectrophotometer. The absorbance decrease of $[\text{Co}(\text{CN})_5\text{NO}_2]^{3-}$ was monitored at $\lambda = 345\text{nm}$ for the redox reaction $\text{Ti}^{\text{III}}/\text{Co}(\text{CN})_5\text{NO}_2^{3-}$, $\lambda = 360\text{nm}$ for both $\text{Ti}^{\text{III}}/\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$ $\text{Ti}^{\text{III}}/\text{Co}(\text{NH}_3)_5\text{ONO}^{2+}$. Constant temperature ($25 \pm 0.1^\circ\text{C}$) was maintained by circulating H_2O from thermostated H_2O bath around the cell compartment of the spectrophotometer. The reactions were monitored at an ionic strength, $I = 1.0\text{ mol dm}^{-3}$ LiCl/HCl. It has been reported earlier that Ti^{3+} has low affinity for Cl^- [13] and the extent of complex formation of Ti^{3+} with chloride is rather small [17] and therefore considered to be a negligible factor in the reactions under investigation.

All the reactions were studied under a pseudo-first order conditions with Ti^{III} in at least 15-fold excess over Co^{III} .

Results and discussion

All the reactions conform to the following rate law:

$$\text{Rate} = k_2[\text{Ti}^{\text{III}}][\text{Co}^{\text{III}}] \quad (1)$$

k_2 is the second-order rate constant for the reaction. The stoichiometric ratio of all the redox reactions was determined to be $\text{Co}^{\text{III}}:\text{Ti}^{\text{III}} = 1:1$. Pseudo-first order plots using the Guggenheim method [18] were linear for more than 80% reaction with slopes k_1 (Tables 1–3). The observed second-order rate constants, k_2 (which are averages of at least triplicate runs) obtained are shown in Tables 1–3. All the reactions showed inverse hydrogen ion dependence.

The rate equation for the reaction can be expressed thus:

$$k_2 \approx k_0 + k[\text{H}^+]^{-1} \quad (2)$$

Table 1. Kinetic data for the reduction of $[\text{Co}(\text{CN})_5\text{NO}_2]^{3-}$ by Ti^{III} at $25 \pm 0.1^\circ\text{C}$, 1.0 mol dm^{-3} (LiCl/HCl)

$[\text{H}^+]$ (mol dm^{-3})	$10^3 [\text{Ti}^{\text{III}}]$ (mol dm^{-3})	$10^4 k_1$ (s^{-1})	Average $k_{2(\text{obs})}$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	Average $k_{2(\text{calcd})}$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)
0.150	4.50	4.43		
	7.50	6.85	0.095	0.103
0.100	4.50	5.86		
	7.50	9.95	0.132	0.146
0.080	4.50	7.56		
	9.00	14.90	0.167	0.175
0.050	2.70	6.723		
	4.50	11.98	0.258	0.280
0.030	2.00	8.911		
	3.00	12.40	0.430	0.420
0.020	1.20	7.98		
	2.40	14.12	0.627	0.615
0.015	1.20	10.71		
	1.60	12.90	0.850	0.801

Table 2. Kinetic data for the reduction of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$ by Ti^{III} at $25 \pm 0.1^\circ\text{C}$, 1.0 mol dm^{-3} (LiCl/HCl)

$[\text{H}^+]$ (mol dm^{-3})	$10^3 [\text{Ti}^{\text{III}}]$ (mol dm^{-3})	$10^4 k_1$ (s^{-1})	Average $k_{2(\text{obs})}$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	Average $k_{2(\text{calcd})}$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)
0.150	6.00	10.98		
	7.50	12.96	0.178	0.187
0.100	6.00	12.16		
	9.00	22.36	0.227	0.243
0.080	2.25	7.27		
	3.75	10.72	0.304	0.291
0.050	2.25	9.98		
	3.75	17.38	0.453	0.440
0.030	2.00	14.90		
	3.00	20.19	0.709	0.688
0.020	1.60	16.67		
	2.40	22.78	0.956	0.991
0.015	1.50	19.02		
	1.60	20.45	1.273	1.284

Table 3. Kinetic data for the reduction of $[\text{Co}(\text{NH}_3)_5\text{ONO}]^{2+}$ by Ti^{III} at $25 \pm 0.1^\circ\text{C}$, 1.0 mol dm^{-3} (LiCl/HCl)

$[\text{H}^+]$ (mol dm^{-3})	$10^3 [\text{Ti}^{\text{III}}]$ (mol dm^{-3})	$10^4 k_1$ (s^{-1})	Average $k_{2(\text{obs})}$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	Average $k_{2(\text{calcd})}$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)
0.150	4.50	8.40		
	7.50	12.95	0.180	0.182
0.100	4.50	12.31		
	9.00	19.62	0.246	0.261
0.080	6.00	17.32		
	9.00	24.71	0.282	0.310
0.050	3.75	17.76		
	4.50	21.38	0.475	0.493
0.030	2.50	18.69		
	3.00	22.45	0.748	0.791
0.020	2.00	22.27		
	2.40	23.38	1.044	1.150
0.015	1.50	23.14		
	1.60	24.64	1.541	1.505

k is a composite rate constant equal to $k'K_a$, where k' is the second order rate constant i.e electron-transfer rate constant for the reduction by TiOH^{2+} , and K_a is the characteristic hydrolytic equilibrium constant for the process.

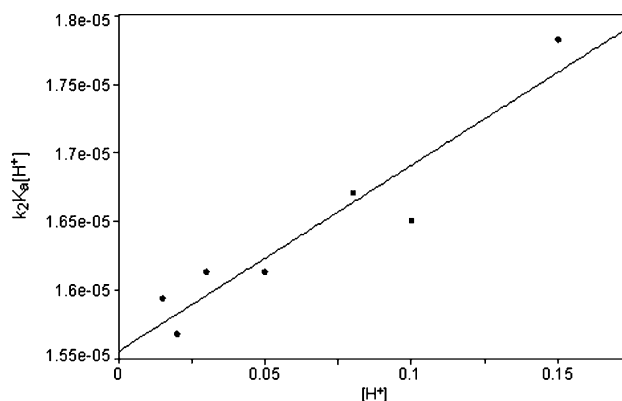


Fig. 1. Plot of $k_2K_a[\text{H}^+]$ against $[\text{H}^+]$ for $\text{Ti}^{\text{III}}/[\text{Co}(\text{CN})_5\text{NO}_2]^{3-}$ using an iterative computer program at $K_a = 1.25 \times 10^{-3} \text{ mol dm}^{-3}$.

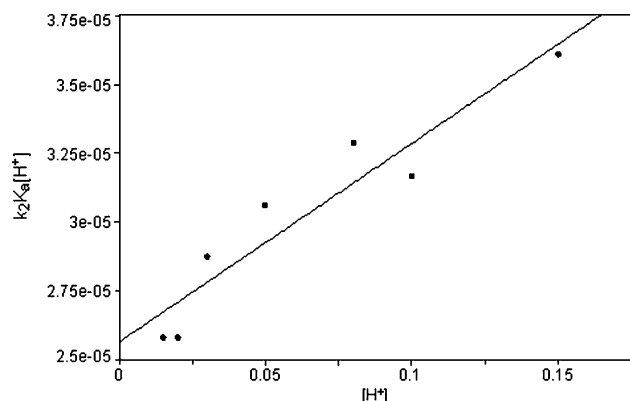


Fig. 2. Plot of $k_2K_a[H^+]$ against $[H^+]$ for $Ti^{III}/[Co(NH_3)_5NO_2]^{2+}$ using an iterative computer program at $K_a = 1.50 \times 10^{-3} \text{ mol dm}^{-3}$.

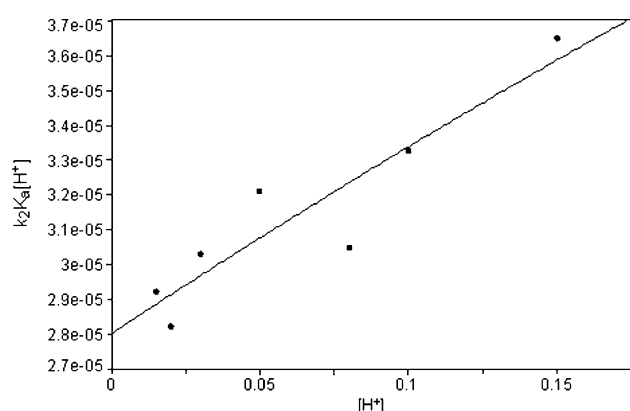
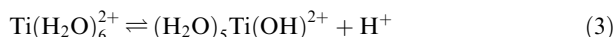


Fig. 3. Plot of $k_2K_a[H^+]$ against $[H^+]$ for $Ti^{III}/[Co(NH_3)_5ONO]^{2+}$ using an iterative computer program at $K_a = 1.50 \times 10^{-3} \text{ mol dm}^{-3}$.



Hence the exact rate law obtained for the reaction is of the form

$$k_2 = \frac{k_0 + k'K_a[H^+]^{-1}}{1 + K_a[H^+]^{-1}} \quad (4)$$

From equation 3 we have:

$$k_2([H^+] + K_a) = k_0[H^+] + k'K_a \quad (5)$$

(where $K_a < [H^+]$ in this study)

Using an iterative computer program and a range of values of K_a , the left-hand side of Equation 4 was plotted against $[H^+]$, which generally gave a straight line with slope k_0 and intercept $k'K_a$ for K_a values in the range $(1 - 2) \times 10^{-3} \text{ mol dm}^{-3}$. The K_a value (Table 4) that gave the best straight line, as indicated by the correlation coefficient, was chosen and hence k_0 and k' were evaluated according to equation 4. Non-negligible k_0 contributions were also observed in all

the reductions of these oxidants by Ti^{III} . Similar observations have been reported in the literature by earlier workers [1, 19–20].

On investigation of the aquation rate of the Co^{III} complexes at 0.1 mol dm^{-3} HCl and 1.0 mol dm^{-3} LiCl in the course of this study, the result obtained revealed that rate of aquation is less than rate of electron transfer *i.e.*, $k_{aq} \ll k_{et}$. The pseudo-first order rate constant at the above acid and ionic concentration is $1.0 \times 10^{-3} \text{ s}^{-1}$ while the aquation rate at this same condition is in the order of 10^{-5} s^{-1} which is very small compared to k_{et} of the reaction. This suggests an outer-sphere mechanism for these reactions. The consistent values of the second-order rate constant k_2 (Tables 1–3) obtained confirms that the reductions of these Co^{III} complexes by Ti^{III} are not adversely affected by the aquation process, *i.e.*, $k_2 = \text{constant}$. Comparing the values of k_0 with k' for all the reactions studied, it is observed that $TiOH^{2+}$ is a much more reactive reductant than Ti^{3+} as indicated by the much larger rate constants k' .

The values of K_a computed from the kinetic data from these redox reactions lie in the range ascribed to outer-sphere reaction mechanisms. Thompson and Sykes [2] gave K_a values of $2 \times 10^{-3} \text{ mol dm}^{-3}$ for the Ti^{III} reduction some Co^{III} complexes and Ojo *et al.* [1] also reported K_a values of $(1.20\text{--}1.80) \times 10^{-3} \text{ mol dm}^{-3}$ for the outer-sphere reductions of the halopentacyano cobaltate(III) complexes by Ti^{III} in acidic aqueous media. K_a values $\geq 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ have been obtained by some workers [19, 21], and such high values have been used to suggest precursor complex formation and hence an inner-sphere mechanism [22]. The ammonia ligands in $[Co(NH_3)_5NO_2]^{2+}$ are more weakly bound to cobalt than the cyano ligands in $[Co(CN)_5NO_2]^{3-}$ [23, 24] and therefore greater reactivity is expected from $[Co(NH_3)_5NO_2]^{2+}$.

The ratio $K_{NH_3}:K_{CN}$ for $[Co(CN)_5NO_2]^{3-}$ and $[Co(NH_3)_5NO_2]^{2+}$ is 1.6:1. This ratio should be large in the event of a non-bridging ligand effect [23–25]. However, the small ratio obtained in this work could be explained by the greater coulombic force of attraction between the negatively charged $[Co(CN)_5NO_2]^{3-}$ and $TiOH^{2+}$ than the repulsion between the positively charged species $[Co(NH_3)_5NO_2]^{2+}$ and $TiOH^{2+}$, which therefore tends to close the reactivity gap.

The ratio of $k_{NO_2^-}:k_{ONO^-}$ for $[Co(NH_3)_5NO_2]^{2+}$ and $[Co(NH_3)_5ONO]^{2+}$ is 1.0:1.2. Though this is very small, but it is significant. This slight difference in the ratio is due to linkage isomerism, suggesting that the Co–ONO bond is weaker than the Co–NO₂ bond.

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Table 4. Summary of k_0 , k' and K_a values

Oxidant	k_0 ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	k' ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	$10^3 K_a$ (mol dm^{-3})
$Co(CN)_5NO_2^{3-}$	1.31 ± 0.50	10.27 ± 0.45	1.25 ± 0.02
$Co(NH_3)_5NO_2^{2+}$	4.53 ± 0.80	14.99 ± 0.70	1.35 ± 0.04
$Co(NH_3)_5ONO^{2+}$	1.70 ± 0.80	17.93 ± 0.78	1.35 ± 0.03

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