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THE REDUCTION OF TRIS(2,4-PENTANEDIONATO) COBALT(III) BY $TiOH^{2+}$ AND $Ti(CH_3COO)^{2+}$ IN AQUEOUS ACIDIC SOLUTION

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ABSTRACT. Aquatitanium(III) reduces $(Co(pd)_3$ (pd = 2,4-pentanedionato ligand) at 25° and $I = 1.0$ mol dm^{-3} (LiCl) with the general rate law:

$$\frac{-d[Co(III)]}{dt} = k_{obs}[Co(III)][Ti(III)]$$

$$where\ \ k_{obs} = \frac{kK}{K + [H^+]}$$

$TiOH^{2+}$ is the effective titanium(III) reductant species with $k = (7.84 \pm 0.89)$ dm^3 mol^{-1} s^{-1} and $K = (0.069 \pm 0.008)$ mol dm^{-3} (k is the rate constant for electron transfer between $Co(pd)_3$ and $TiOH^{2+}$ and K is a composite equilibrium quotient). The magnitude of K and the enhanced reactivity of $Co(pd)_3$ with the effective reductant as indicated by the log-log plots (based on Marcus Linear Free Energy Relationship) suggest inner-sphere mechanism for the reaction. $Ti(CH_3COO)^{2+}$ generated *in-situ* by adding excess acetate ions to aquatitanium(III) reduces $Co(pd)_3$ much slower than does $TiOH^{2+}$ ($k_{Ti(CH_3COO)^{2+}} = (0.39 \pm 0.04)$ dm^3 mol^{-1} s^{-1}).

INTRODUCTION

Tris(2,4-pentanedionato) cobalt(III), $Co(pd)_3$, is reduced by V^{2+} and Eu^{2+} via outer-sphere mechanism while it is reduced by Cr^{2+} via parallel outer-sphere and inner-sphere pathways [1]. Though 2,4-pentanedione coordinates [2] with aquatitanium(III) via the keto-enol equilibrium, $Ru(pd)_3$ is reduced [3] by aquatitanium(III) via the outer-sphere pathway. We hereby report the reduction of $Co(pd)_3$ by Ti(III). The mechanistic and rate differences often observed [1-5] in the reactivities of Ru(III) and Co(III) complexes and interpreted in terms of the orbital spin difference between the two metal ions, is again exhibited in this report.

$Ti(CH_3COO)^{2+}$ generated *in-situ* [6] from the addition of excess acetate ions to aquatitanium(III), reduces $Co(pd)_3$ much slower than $TiOH^{2+}$. An explanation is suggested for this inhibition which is in contrast with catalysis observed for similar aquatitanium(III) oxidations in the presence of added oxalate and ethylenediamine tetraacetate ions [7-9].

EXPERIMENTAL

Materials. Acidic solutions of Ti(III) were prepared by dissolving titanium metal in approximately 6 mol dm^{-3} HCl at about 50° for a period of 36 hrs, stirring with a magnetic stirrer in an inert nitrogen atmosphere. The solutions were standardised with respect to the metal ion, Ti(III), and free acid, H^+ concentrations as in the literature [10]. LiCl (Hopkins and Williams reagent grade) was recrystallised twice and the HCl used was of Analar grade.

Tris(2,4-pentanedionato)cobalt(III), $Co(pd)_3$, was synthesised as previously described [11], and its UV-VIS spectrum showed peaks at 600 nm (ϵ = 125 dm^3 mol^{-1} cm^{-1}) and 328 nm (ϵ = 7600 dm^3 mol^{-1} cm^{-1})in agreement with literature values.

Kinetics. Rate measurements were made by following absorbance changes in the $Co(pd)_3$ solution at 340 nm (ϵ = 6200 dm^3 mol^{-1} cm^{-1}) on a Pye Unicam SP6 - 500 UV-VIS spectrophotometer. Reactions were monitored under pseudo first-order conditions, with the Ti(III) concentrations in at least ten-fold excess over the Co(III) concentrations.

All kinetic measurements were made in nitrogen atmosphere to avoid air-oxidation of Ti(III) [6] and ionic strength was maintained at 1.0 mol dm^{-3} LiCl (and not $LiClO_4$) as ClO_4^- is known to oxidise Ti(III) [6, 9, 12-15]. Temperature was maintained at (25.0 ± 0.1)° by circulating water round the cell compartment from a well-thermostated water bath.

RESULTS

The stoichiometry of each reaction was checked by spectrophotometric titrations and confirmed to be 1 mole of $Co(pd)_3$ consumed by 1 mole of the Ti(III) complex both in the presence and absence of the acetate ion. The kinetic data are listed in Tables 1 and 2. From Table 1, it is observed that at constant free acid concentration, there is no large or systematic variation in the values of the second-order rate constants (k_{obs}). This follows a general rate law of the type:

$$Rate = \frac{-d[Co(pd)_3]}{dt} = k_{obs}[Co(pd)_3]\ [Ti(III)] \tag{1}$$

It is however observed that k_{obs} varies inversely with free acid concentration, such that a plot of k_{obs}^{-1} against $[H^+]$ (Figure 1) is linear. This is consistent with the rate expression:

$$k_{obs} = \frac{kK}{K + [H^+]} \tag{2}$$

The values of k and K obtained, employing least-square fit to the plot of k_{obs}^{-1} against $[H^+]$ are:

$k = (7.84 \pm 0.89)$ dm^3 mol^{-1} s^{-1}
$K = (0.069 \pm 0.008)$ mol dm^{-3}

When acetate ion is added to the aquatitanium(III) reductant, an additional reductant species, $Ti(CH_3COO)^{2+}$ is formed. The important equilibria in this connection are:

$$Ti^{3+} + H_2O \rightarrow TiOH^{2+} + H^+ \quad K_A = \frac{[TiOH^{2+}]\ [H^+]}{[Ti^{3+}]} \tag{3}$$

$$CH_3COOH \rightarrow CH_3COO^- + H^+ \qquad K_B = \frac{[CH_3COO^-]\,[H^+]}{[CH_3COOH]} \tag{4}$$

$$Ti^{3+} + CH_3COO^- \rightarrow Ti(CH_3COO)^{2+} \qquad K_C = \frac{[Ti(CH_3COO)^{2+}]}{[Ti^{3+}]\,[CH_3COO^-]} \tag{5}$$

Table 1. Kinetic data for the reduction of $Co(pd)_3$ by aqua-Ti(III) in 1.0 mol.dm^{-3} (LiCl) and at (25.0 ± 0.10)°.

$[H^+]$ mol dm^{-3}	$10^5[Co(pd)_3]$ mol dm^{-3}	$10^4[Ti(III)]$ mol dm^{-3}	10^4k_s s^{-1}	k_{obs} dm^3 mol^{-1} s^{-1}
0.005	2.00	2.00	13.67	6.83
	2.00	2.05	15.80	7.70
	2.00	3.00	22.00	7.50
0.008	1.83	1.98	13.73	6.92
	1.85	1.98	13.29	6.70
	2.00	2.05	14.51	7.08
0.010	1.83	1.98	11.25	5.67
	1.83	2.00	12.70	6.35
	1.83	3.00	19.05	6.35
	1.83	4.00	24.60	6.15
0.025	1.83	1.98	11.30	5.71
	1.83	2.00	10.55	5.28
	1.83	2.05	11.30	5.51
	1.83	4.00	22.00	5.50
0.050	1.83	1.96	8.03	4.09
	1.83	1.98	10.00	5.06
	1.83	3.00	12.95	4.32
	1.83	4.00	15.70	3.92
0.075	1.83	1.96	7.34	3.74
	1.83	1.98	7.08	3.57
	1.83	2.00	7.65	3.83
0.100	1.83	1.96	6.67	3.40
	1.83	1.98	5.81	2.98
	1.83	2.00	7.00	3.50
	2.00	2.05	6.00	2.92
	1.83	3.00	9.84	3.28
	1.83	4.00	12.35	3.09
	2.00	6.00	19.08	3.18
	2.00	10.0	32.00	3.20

Table 2. Kinetic data for the reduction of $Co(pd)_3$ by $Ti(CH_3COO)^{2+}$ in 10 mol dm^{-3} (LiCl) and at (25.0 ± 0.1)°[a].

$10^3[H^+]_f$ mol dm^{-3}	$10^3[H^+]_T$ mol dm^{-3}	$10^4[CH_3COO^-]$ mol dm^{-3}	k_{obs} dm^3 mol^{-1} s^{-1}	B dm^3 mol^{-1} s^{-1}
100	100.2	2.0	1.55	6.34
100	100.3	3.0	1.28	6.77
100	100.4	4.0	1.11	7.20
100	100.6	6.0	0.91	8.08
100	100.8	8.0	0.81	9.14
100	101.0	10.0	0.73	9.99

[a] $[CO(pd)_3]$ = (1.885 - 2.00) x 10^{-4} mol dm^{-3}; $[Ti(III)]$ = 2.0 x 10^{-4} mol dm^{-3}

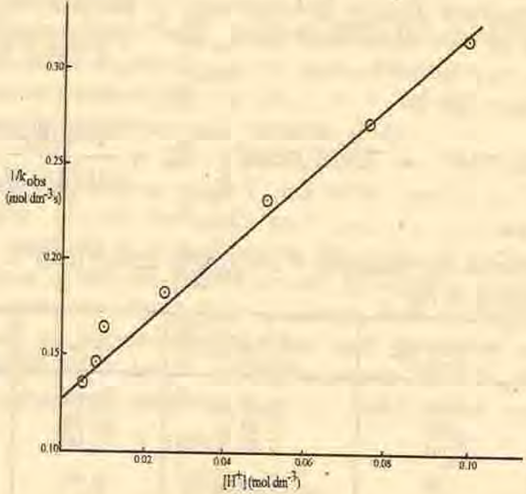

Figure 1. Plot of $1/k_{obs}$ *vs* $[H]^+$

Chaudhuri and Diebler [6] measured K_B and k_c as 3.4×10^{-5} mol dm^{-3} and 390 dm^3 mol^{-1}, respectively at 15° and 0.5 mol dm^{-3} ionic strength (LiCl).

In the presence of this added acetate, the competing redox reactions are:

$$Ti^{3+} + Co(pd)_3 \xrightarrow{k_0} products \tag{6}$$

$$TiOH^{2+} + Co(pd)_3 \xrightarrow{k_1} products \tag{7}$$

$$Ti(CH_3COO)^{2+} + Co(cp)_3 \xrightarrow{k_1} products \tag{8}$$

From the aquatitanium(III)/Co(pd)$_3$ reaction, TiOH^{2+} is the only active reductant (i.e. $k_o \approx 0$). Therefore treatment of Equations 6 to 8 leads to a rate expression given by:

$$\frac{-d[Co(III)]}{dt} = k[TiOH^{2+}] + k_1[Ti(CH_3COO)^{2+}] = k_s$$

$$= k_{obs}\,[Ti(III)]_T \tag{9}$$

where, k_s is the pseudo-first order rate constant and $[Ti(III)]_T$ the total Ti(III) concentration and k_{obs} is given as:

$$k_{obs} = \frac{kK[H^+]^{-1} + k_1K_CL}{1 + K[H^+]^{-1} + K_CL} \tag{10}$$

where, L is the free acetate ion concentration.

Rearrangement of Equation 10 gives:

$$k_{obs}(1+K[H^+]^{-1} + K_cL) = kK[H^+]^{-1} + k_1K_cL \tag{11}$$

Using our values of k_{obs} and K, an iterative computer programme was used to obtain other parameters listed in Table 2. Our computed value of 1100 $dm^3\ mol^{-1}$ for K_c differs from Chaudhuri and Diebler's value [6] of 390 $dm^3\ mol^{-1}$. This disagreement might have emanated from the different experimental conditions. From a plot of the left hand side of Equation 11 (denoted by B in Table 2) against L, values of k (7.78 $dm^3\ mol^{-1}\ s^{-1}$) and k_1 (0.39 $dm^3\ mol^{-1}\ s^{-1}$) are obtained from the slope and intercept, respectively. The value of k (7.78 ± 0.81 $dm^3\ mol^{-1}\ s^{-1}$) obtained here is in good agreement with the previous value of $k_{TiOH^{2+}}$ (7.84 ± 0.89 $dm^3\ mol^{-1}\ s^{-1}$) obtained in the absence of acetate ions.

DISCUSSION

The value of K obtained (0.069 mol dm^{-3}) from the electron transfer reaction between Ti(III) and tris(2,4-pentanedionato) cobalt(III) is about 35 times greater than would be expected for simple deprotonation of Ti^{3+} in which K_a is 2 x 10^{-3} mol dm^{-3} [7, 11, 13]. A scheme consistent with the data can therefore be expressed as in Equations 12 to 15.

$$Co^{III}(pd)_3 + Ti^{3+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (pd)_2Co^{III}(pd)Ti^{3+} \tag{12}$$

$$(pd)_2Co^{III}(pd)Ti^{3+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (pd)_2Co^{III}(pd)TiOH^{2+} + H^+ \tag{13}$$

$$(pd)_2Co^{III}(pd)TiOH^{2+} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} (pd)_2Co^{II}(pd)Ti^{IV}OH^{2+} \tag{14}$$

$$(pd)_2CO^{II}(pd)Ti^{IV}OH^{2+} \xrightarrow{fast} products \tag{15}$$

Similar schemes had previously been proposed for the $Co(NH_3)_4C_2O_4^+$, $Ru(C_2O_4)_3^{3-}$ and $(NH_3)_5RuX^+$ (X = SO_4^{2-}, $S_2O_3^{2-}$, etc.) reductions by Ti(III) [7, 8, 16] which involve unstable precursor complexes. The electron transfer (ET) rate constant at 25°, I = 1.0 mol dm^{-3} (LiCl) for the Ti(III)/Co(pd)$_3$ system (k = 7.84 ± 0.89 $dm^3\ mol^{-1}\ s^{-1}$) is much smaller than those previously [8, 10, 15] ascribed to substitution-controlled ET processes. The rate of substitution reactions of Ti(III) have been reported to be dependent on the charge of the entering group [7, 12].

Since Co(pd)$_3$ is uncharged, the relatively low ET rate constant obtained in this study cannot therefore be entirely ascribed to a substitution-controlled step, and so the deprotonation and ET steps, (13) and (14), respectively, must be rate-determining to some extent as well.

The redox rate constants for the reduction of some Co(III) complexes by $TiOH^{2+}$ and V^{2+} were subjected to the modified Marcus equation plots [15, 17, 18] (Figure 2). Based on the plot, these reactions (with the exception of $[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$ reduction presented by H on the plot) had been suggested to occur by the outer-sphere mechanism. The V^{2+}

reduction of $Co(pd)_3$ was also suggested to be by this outer-sphere mechanism [1]. The point representing the present reaction (I) lies above the line in Figure 2 and hence an inner-sphere mechanism is suggested for the reduction of $Co(pd)_3$ by $TiOH^{2+}$. Furthermore, Linck and Sullivan [1] had proposed a parallel outer- and inner-sphere mechanism for the Cr^{2+} reduction of $Co(pd)_3$ at high acidity (2 mol dm^{-3} $HClO_4$) saying that the inner-sphere percentage increased with decreasing acidity. Considering the low acid (highest is 0.1 mol dm^{-3}) employed in this work, our inner-sphere mechanism is in excellent agreement with the earlier observation [1].

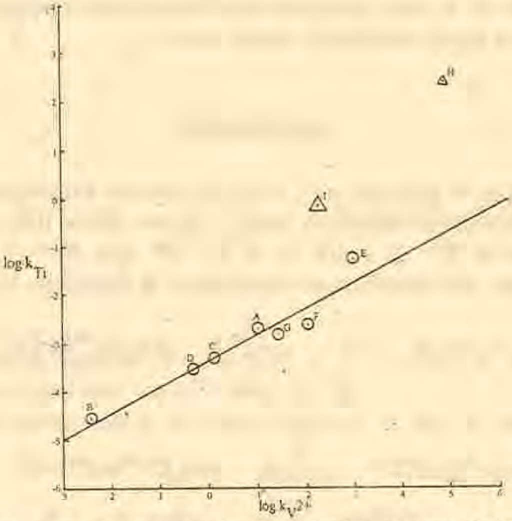

Figure 2. Log-log plot for the reduction of some Co(III) complexes by $TiOH^{2+}$ and V^{2+} [15] (I = this work).

It has been reported that the addition of non-bridging oxalate [7, 8, 9], EDTA [19, 20, 21] and 2,4-pentanedionato [9] ligands onto Ti(III) have consistently catalysed the reactions of Ti(III) with Co(III) and Ru(III) complexes. In the present system, the effect of added acetate ion on Ti(III) as a non-bridging ligand has caused inhibition, an observation opposite to the earlier ones. A somehow similar slower intramolecular electron transfer was observed [22] in some Ti(III) - Co(III) and Ti(III) - Ru(III) reactions but involving bigger dihydroxyquinone dianion as a bridging ligand. A plausible explanation of our present observation can be ascribed to the reduction in the oxidation potential of Ti(III) in the presence of added acetate [23]; i.e. $Ti(CH_3COO)^{2+}$ is expected to be less reactive than $TiOH^{2+}$ as has been demonstrated in this study.

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