THE REDUCTION OF TRIS(2,4-PENTANEDIONATO) COBALT(III) BY TiOH$^{2+}$ AND Ti(CH$_3$COO)$^{2+}$ IN AQUEOUS ACIDIC SOLUTION

Olayinka Oyetunji$^1$, J. Folorunso Ojo$^2$ and Olusegun Obubuyide$^2$

$^1$Department of Chemistry, University of Zimbabwe, Mount Pleasant Harare, Zimbabwe, $^2$Department of Chemistry, Obafemi Awolowo University, Ile-Ife, Nigeria

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ABSTRACT. Aquatitanium(III) reduces Co(pd)$_3$ (pd = 2,4-pentanedionato ligand) at 25$^\circ$ 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$_3$COO)$^{2+}$ generated in-situ by adding excess acetate ions to aquatitanium(III) reduces Co(pd)$_3$ much slower than does TiOH$^{2+}$ ($k_{Ti(CH_3COO)}$ = (0.39 ± 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 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$_3$COO)$^{2+}$ 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$^\circ$ 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 Analalr 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 dm³ mol⁻¹ cm⁻¹) and 328 nm (ε = 7600 dm³ 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 dm³ 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 LiClO₄) as ClO₄⁻ 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 (k₀ᵇˢ). This follows a general rate law of the type:

\[
Rate = \frac{-d[Co(pd)₃]}{dt} = kₐᵢₜ[Co(pd)₃][Ti(III)]
\]  

(1)

It is however observed that kᵦᵢₜ varies inversely with free acid concentration, such that a plot of kₐᵢₜ⁻¹ against [H⁺] (Figure 1) is linear. This is consistent with the rate expression:

\[
kₐᵢₜ = \frac{kK}{K + [H^+]}\]

(2)

The values of k and K obtained, employing least-square fit to the plot of kₐᵢₜ⁻¹ against [H⁺] are:

\[
k = (7.84 ± 0.89) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}
\]

\[
K = (0.069 ± 0.008) \text{ mol dm}^3
\]

When acetate ion is added to the aquatitanium(III) reductant, an additional reductant species, Ti(CH₃COO)²⁺ is formed. The important equilibria in this connection are:

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

(3)
The reduction of tris(2,4-pentanedionato) cobalt(III) 

\[
CH_3COOH \rightarrow CH_3COO^- + H^+ \quad K_B = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \quad (4)
\]

\[
Ti^{3+} + CH_3COO^- \rightarrow Ti(CH_3COO)^{2+} \quad K_C = \frac{[Ti(CH_3COO)^{2+}]}{[Ti^{3+}][CH_3COO^-]} \quad (5)
\]

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)$^\circ$.

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<th>$10^4[Co(pd)_3]$ mol dm$^{-3}$</th>
<th>$10^4[Ti(III)]$ mol dm$^{-3}$</th>
<th>$10^4k$ s$^{-1}$</th>
<th>$k_{obs}$ dm$^3$ mol$^{-1}$ s$^{-1}$</th>
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Table 2. Kinetic data for the reduction of Co(pd)$_3$ by Ti(CH$_3$COO)$^{2+}$ in 10 mol dm$^{-3}$ (LiCl) and at (25.0 ± 0.1)$^\circ$.

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<th>$10^4[H^+]_2$ mol dm$^{-3}$</th>
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<th>$k_{obsi}$ dm$^3$ mol$^{-1}$ s$^{-1}$</th>
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$^[CO(pd)_3] = (1.885 - 2.00) \times 10^4$ mol dm$^{-3}$, $[Ti(III)] = 2.0 \times 10^4$ mol dm$^{-3}$
Chaudhuri and Diebler [6] measured $K_B$ and $k_c$ as $3.4 \times 10^{-5}$ 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:

$$Ti^{3+} + Co(pd)_3 \rightarrow \text{products}$$ \hspace{1cm} (6)

$$TiOH^{2+} + Co(pd)_3 \rightarrow \text{products}$$ \hspace{1cm} (7)

$$Ti(CH_3COO)^{2+} + Co(cp)_3 \rightarrow \text{products}$$ \hspace{1cm} (8)

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

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

$$= k_{obs} [Ti(III)]_T$$ \hspace{1cm} (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:

$$k_{obs} = \frac{kK[H^+]^{-1} + k_1K_cL}{1 + K[H^+]^{-1} + K_cL}$$ \hspace{1cm} (10)

where, $L$ is the free acetate ion concentration.

Rearrangement of Equation 10 gives:
\[ k_{\text{obs}}(1 + K[H^+])^{-1} + K_cL = kK[H^+]^{-1} + k_1K_cL \]  \hspace{1cm} (11)

Using our values of \( k_{\text{obs}} \) and \( K_c \), 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 \( k_c \) (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 \( k_c \) (7.78 ± 0.81 dm\(^3\) mol\(^{-1}\) s\(^{-1}\)) obtained here is in good agreement with the previous value of \( k_{\text{ion}} \) (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 \( K_c \) 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.

\[ \text{Co}^{III}(pd)_3 + \text{Ti}^{3+} \xrightleftharpoons[k_{-1}]{k_1} (pd)_2\text{Co}^{III}(pd)\text{Ti}^{3+} \]  \hspace{1cm} (12)

\[ (pd)_2\text{Co}^{III}(pd)\text{Ti}^{3+} \xrightleftharpoons[k_2]{k_{-2}} (pd)_2\text{Co}^{III}(pd)\text{TiOH}^{2+} + H^+ \]  \hspace{1cm} (13)

\[ (pd)_2\text{Co}^{III}(pd)\text{TiOH}^{2+} \xrightleftharpoons[k_3]{k_{-3}} (pd)_2\text{Co}^{II}(pd)\text{Ti}^{IV}OH^{2+} \]  \hspace{1cm} (14)

\[ (pd)_2\text{CO}^{II}(pd)\text{Ti}^{IV}OH^{2+} \xrightarrow{\text{fast}} \text{products} \]  \hspace{1cm} (15)

Similar schemes had previously been proposed for the Co(NH\(_3\))\(_2\)C\(_2\)O\(_4\)\(^{3+}\), Ru(C\(_2\)O\(_4\))\(_3\)\(^{3-}\) and (NH\(_3\))\(_2\)RuX\(^+\) (X = SO\(_4\)^{2-}, S\(_2\)O\(_8\)^{2-}, \text{etc.}) reductions by Ti(III) [7, 8, 16] which involve unstable precursor complexes. The electron transfer (ET) rate constant at 25\(^\circ\), \( I = 1.0 \) mol dm\(^{-3}\) (LiCl) for the Ti(III)/Co(pd)_3 system \((k = 7.84 ± 0.89 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})\) 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\(_3\))\(_2\)CoO\(_2\)Co(NH\(_3\))\(_4\)]\(^{3+}\) 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$^{3+}$ 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).](image)

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 somewhat 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$_3$COO)$_2^{2+}$ is expected to be less reactive than TiOH$^{2+}$ as has been demonstrated in this study.

**ACKNOWLEDGEMENTS**

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REFERENCES