(29) The bridging N–H groups of compound II do not exchange with solvent or with the C_5H_5 ligands.

(30) This should be regarded as a lower limit. Since we had to analyze for CO_2 in the presence of HCl, $(C_2H_5)_3N$ was used to absorb the HCl. The CO_2 was then collected with the Toepler pump. It is very difficult to collect all the CO_2 because of the solubility of CO_2 in amines.

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Contribution from the Department of Chemistry,
University of Ife, Ile-Ife, Nigeria

Mechanisms of the Titanium(III) Reduction of Tris(1,10-phenanthroline)cobalt(III), Tris(oxalato)cobaltate(III), and Tris(1,10-phenanthroline)iron(III) in Aqueous Solutions

NIYI AKINYUGHA, JIDE IGE, J. FOLORUNSO OJO,* OLUSEGUN OLUBUYIDE, and R. SIMOYI

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The reduction of tris(1,10-phenanthroline)cobalt(III), tris(oxalato)cobaltate(III) and tris(1,10-phenanthroline)iron(III) by titanium(III) in aqueous solutions has been studied at 25 °C, $I = 1.0$ mol dm^{-3} (LiCl). The dependence of the second-order rate constants, k_{obsd}, on $[H^+]$ has been investigated over the range 0.05–1.00 mol dm^{-3}, and the rate constant is of the form $k_{obsd} = k_0 + k_1[H^+]^{-1}$ for tris(1,10-phenanthroline)cobalt(III). The $[H^+]$ dependence for tris(oxalato)cobaltate(III) and tris(1,10-phenanthroline)iron(III) is of the form $1/k_{obsd} = a + b[H^+]$. The magnitudes of the parameters a and b for tris(oxalato)cobaltate(III) are indicative of precursor complex formation, attributed to chelation of $TiOH^{2+}$ by oxalate ligand. The magnitudes of a and b for tris(1,10-phenanthroline)iron(III) do not indicate precursor complex formation. Observed catalytic effects of added anions and calculations based on the Marcus equation on the reaction of tris(1,10-phenanthroline)cobalt(III) and tris(1,10-phenanthroline)iron(III) suggest that they react with titanium(III) by outer-sphere mechanisms.

Assignment of mechanism to redox reactions involving titanium(III) has been based on usual criteria applied to other reductants, viz., relative rates[1,2] (k_{N_3}/k_{NCS}), electron mediating ability of carboxylate groups[3a,3b] through conjugation and/or chelation, and log–log plots using Marcus linear free energy relationships.[4] Inverse hydrogen ion dependence[1–8] of observed second-order rate constants has dominated the kinetics of aqueous reactions of titanium(III), and the nature of this has been used recently in some cases to suggest precursor complex formation and hence inner-sphere mechanisms. The complex nature of the inverse hydrogen-ion dependence observed in certain cases makes alternative[2,8] or parallel reaction paths possible. Thus, while Orhanovic and Earley[8] were unable to assign a mechanism to the reactions of titanium(III) with $Co(NH_3)_5Cl^{2+}$ and *cis*- and *trans*-$Co(en)_2Cl_2^+$, Thompson and Sykes[4] were able to use log–log plot correlations to assign an outer-sphere mechanism to these reactions. We here report a study utilizing some of the above criteria, as well as current ideas on the characteristic hydrolytic behavior of titanium(III), to assign mechanisms to its reactions with tris(1,10-phenanthroline)cobalt(III), tris(oxalato)cobaltate(III), and tris(1,10-phenanthroline)iron(III).

Experimental Section

Materials. $LiClO_4$ was prepared and recrystallized several times by standard procedures.[9]

LiCl (Hopkin and Williams Reagent grade) was recrystallized twice. The hydrochloric acid was Analar grade reagent. Pure titanium(III) chloride (Koch-Light Laboratories, Ltd.) was used. Fresh Ti(III) solutions, prepared and stored at 0 °C each day before use, were standardized as described[2] previously.

The complexes $Co(phen)_3^{3+}$, $Co(C_2O_4)_3^{3-}$, and $Fe(phen)_3^{3+}$ were prepared and recrystallized as described in the literature.[10,11] Their UV–visible spectra were in good agreement with literature[12–14] values. $Co(C_2O_4)_3^{3-}$ was kept in a tube wrapped with aluminum foil to avoid photolysis. $Fe(phen)_3^{3+}$ solutions in 5 mol dm^{-3} perchloric acid were freshly prepared each day and kept in ice before use.

Kinetics. The fast reactions of Ti(III) with $Co(C_2O_4)_3^{3-}$ and $Fe(phen)_3^{3+}$ were monitored on a Durrum-Gibson stopped-flow spectrophotometer. Decreasing absorbance of $Co(C_2O_4)_3^{3-}$ was followed[13] at λ 605 nm (ε 175 dm^3 mol^{-1} cm^{-1}) for the Ti(III)–$Co(C_2O_4)_3^{3-}$ reaction; increasing absorbance of $Fe(phen)_3^{2+}$ produced in the Ti(III)–$Fe(phen)_3^{3+}$ reaction was followed[14] at λ 510 nm (ε 1.09 × 10^4 dm^3 mol^{-1} cm^{-1}). The slow Ti(III)–$Co(phen)_3^{3+}$ reaction was followed on an SP 500 spectrophotometer. The reductant was always in large excess (≥tenfold). All runs were performed at 25.0 ± 0.1 °C in chloride media, with $I = 1.0$ mol dm^{-3} (LiCl). The use of perchlorate was avoided due to complications arising from its reactions with Ti(III).[3a] However, where effects of chloride were investigated, $LiClO_4$ was used to maintain the ionic strength at 1.0 mol dm^{-3}. Perchlorate was introduced via the oxidant solution. Pseudo-first-order rate plots were linear to more than 85% reaction in all cases.

Results

Stoichiometry was checked for each of the reactions by recording the UV–visible spectra of the reaction mixtures before and after each reaction. The results were consistent with the reduction of 1 mol of oxidant by 1 mol of Ti(III). Each reaction could therefore be written as

$$\mathrm{Ti(III)} + \mathrm{M(III)} \rightarrow \mathrm{Ti(IV)} + \mathrm{M(II)} \tag{1}$$

where M = Co or Fe. The reactions obey the rate law

$$\text{rate} = k_{obsd}[\mathrm{Ti(III)}][\mathrm{M(III)}] \tag{2}$$

Second-order rate constants k_{obsd} are listed in the tables.

Ti(III)–$Co(phen)_3^{3+}$ Reaction. The dependence of k_{obsd} on $[H^+]$ was investigated in the range 0.05–1.00 mol dm^{-3} (Table I) and is of the form

$$k_{obsd} = k_0 + k_1[H^+]^{-1} \tag{3}$$

with $k_0 = 0.038 \pm 0.009$ dm^3 mol^{-1} s^{-1} and $k_1 = 0.24 \pm 0.04$ s^{-1}.

Thompson and Sykes[4] have used the equation in the form

$$k_{obsd} = k_1/(K_a + [H^+]) \tag{4}$$

to make more precise evaluation of k_1, where K_a is the hydrolysis constant for Ti^{3+}:

$$Ti^{3+} + H_2O \overset{K_a}{\rightleftharpoons} TiOH^{2+} + H^+ \tag{5}$$

A good fit of their data to eq 4 was found for the Co(III)

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Table I. Rate Constants, k_{obsd}, for the Ti(III) Reduction of $Co(phen)_3^{3+}$, $Co(C_2O_4)_3^{3+}$, and $Fe(phen)_3^{3+}$ at 25 °C, I = 1.00 mol dm^{-3} (LiCl)

$Co(phen)_3^{3+}$
[Ti(III)] = (0.94–2.47) × 10^{-3} mol dm^{-3};
[$Co(phen)_3^{3+}$] = (1.0–2.0) × 10^{-5} mol dm^{-3}
λ 350 nm (ε 3605 dm^3 mol^{-1} cm^{-1})

$[H^+]$, mol dm^{-3}	k_{obsd}, dm^3 mol^{-1} s^{-1}	k_{calcd},[a] dm^3 mol^{-1} s^{-1}	$[H^+]$, mol dm^{-3}	k_{obsd}, dm^3 mol^{-1} s^{-1}	k_{calcd},[a] dm^3 mol^{-1} s^{-1}
0.050	5.0	4.8	0.400	0.74	0.65
0.055	4.3	4.4	0.500	0.72	0.56
0.063	3.7	3.9	0.600	0.48	0.46
0.080	3.0	3.0	0.700	0.39	0.40
0.100	2.6	2.4	0.750	0.31	0.38
0.125	1.9	2.0	0.850	0.29	0.34
0.150	1.7	1.7	0.950	0.27	0.31
0.200	1.2	1.3	1.00	0.25	0.30

$Co(C_2O_4)_3^{3-}$
[Ti(III)] = (5.2–12.0) × 10^{-3} mol dm^{-3};
[$Co(C_2O_4)_3^{3-}$] = (3.3–3.8) × 10^{-4} mol dm^{-3}

$[H^+]$, mol dm^{-3}	10^{-3} × k_{obsd}, dm^3 mol^{-1} s^{-1}	10^{-3} × k_{calcd},[b] dm^3 mol^{-1} s^{-1}	$[H^+]$, mol dm^{-3}	10^{-3} × k_{obsd}, dm^3 mol^{-1} s^{-1}	10^{-3} × k_{calcd},[b] dm^3 mol^{-1} s^{-1}
0.05	1.5	1.3	0.40	0.39	0.39
0.06	1.2	1.2	0.50	0.30	0.32
0.08	1.1	1.1	0.60	0.27	0.28
0.10	0.80	0.95	0.75	0.24	0.24
0.25	0.58	0.55	0.90	0.21	0.19
			1.00	0.16	0.18

$Fe(phen)_3^{3+}$
[Ti(III)] = (6.18–24.7) × 10^{-4} mol dm^{-3};
[$Fe(phen)_3^{3+}$] = (2.0–4.0) × 10^{-5} mol dm^{-3}

$[H^+]$, mol dm^{-3}	10^{-5} × k_{obsd}, dm^3 mol^{-1} s^{-1}	10^{-5} × k_{calcd},[b] dm^3 mol^{-1} s^{-1}	$[H^+]$, mol dm^{-3}	10^{-5} × k_{obsd}, dm^3 mol^{-1} s^{-1}	10^{-5} × k_{calcd},[b] dm^3 mol^{-1} s^{-1}
0.05	3.3	3.4	0.20	1.3	1.3
0.06	3.1	3.0	0.37	0.80	0.80
0.10	2.2	2.2	0.50	0.55	0.60
0.11	2.1	2.1	0.67	0.44	0.44
0.17	1.5	1.5	0.80	0.38	0.37

[a] From eq 3 and computed values of k_0 and k_1. [b] From eq 6 and computed values of a and b.

complexes studied[4] with $K_a = 2 \times 10^{-3}$ mol dm^{-3} except for $Co(NH_3)_5F^{2+}$ requiring $K_a \gg 2 \times 10^{-3}$ mol dm^{-3}. For the Ti(III)–$Co(phen)_3^{3+}$ reaction, our data fit eq 6 which is of the

$$1/k_{obsd} = a + b[H^+] \qquad (6)$$

same form as eq 4 with $a = K_a/k_1$ and $b = 1/k_1$, where K_a and k_1 have the values (1.52 ± 0.34) × 10^{-3} mol dm^{-3} and 0.25 ± 0.03 s^{-1}, respectively. The effect of added chloride was investigated in the range 0.11–1.00 mol dm^{-3}, and it was found (Table II) that it has a slight accelerating effect on the reaction.

Reactions of Ti(III) with $Co(C_2O_4)_3^{3-}$ and $Fe(phen)_3^{3+}$. In the acid range investigated (Table I), observed second-order rate constants give a good fit to eq 6—see Figures 1 and 2. Plots of k_{obsd} against $[H^+]^{-1}$ gave curves. The values of a and b computed from the data are the following: ($Co(C_2O_4)_3^{3-}$) a = (5.30 ± 0.22) × 10^{-4} mol dm^{-3} s, b = (5.19 ± 0.20) × 10^{-3} s; ($Fe(phen)_3^{3+}$) a = (0.14 ± 0.04) × 10^{-5} mol dm^{-3} s, b = (3.17 ± 0.05) × 10^{-5} s. Since eq 6 is essentially of the same form as eq 4, values of a and b obtained here imply that K = (0.102 ± 0.012) mol dm^{-3} for $Co(C_2O_4)_3^{3-}$ and K_a = (0.043 ± 0.006) mol dm^{-3} for $Fe(phen)_3^{3+}$. (K is used for the Ti(III)–$Co(C_2O_4)_3^{3-}$ reaction (instead of K_a, the hydrolysis constant for Ti^{3+}) since its value lies outside the range of values usually obtained for K_a.)

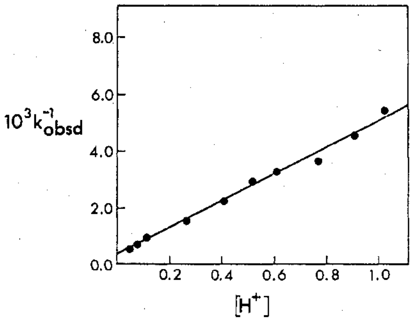


Figure 1. Acid dependence of the rate constants for the Ti(III)–$Co(C_2O_4)_3^{3-}$ reaction. Plot of $1/k_{obsd}$ vs. $[H^+]$.

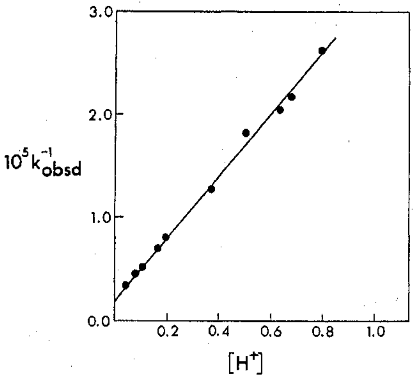


Figure 2. Acid dependence of the rate constants for the Ti(III)–$Fe(phen)_3^{3+}$ reaction. Plot of $1/k_{obsd}$ vs. $[H^+]$.

The effects of added anions on the reactions were also investigated. Added chloride has no detectable effect on the Ti(III)–$Co(C_2O_4)_3^{3-}$ reaction, but added chloride and bromide have a marked accelerating effect on the Ti(III)–$Fe(phen)_3^{3+}$ reaction. Bromide has the greater accelerating effect (Table II).

Discussion

The $[H^+]$ dependence of the reaction of Ti(III) with $Co(phen)_3^{3+}$ may be described in terms of eq 3, in agreement with the results obtained for the reactions of Ti(III) with $Co(bpy)_3^{3+}$, $Co(NH_3)_5SO_4^+$, $Co(NH_3)_6^{3+}$, etc., earlier reported by Thompson and Sykes.[4] The data obtained imply that $TiOH^{2+}$ is the predominant reactive Ti(III) species, with a small contribution from Ti^{3+}. Varying values of K_a have been reported by many workers, presumably because of the different media used and different ionic strengths employed. Pecsok and Fletcher, for instance, measured[15] K_a spectrophotometrically as 0.012 mol dm^{-3} (I = 0.50 mol dm^{-3} KBr) or 0.015 mol dm^{-3} (I = 0.50 mol dm^{-3} (LiCl)); whereas others have deduced the value of K_a from a kinetic data fit, giving values varying between 1.6 × 10^{-3} mol dm^{-3} (Krentzien and Brito,[16] I = 3.0 mol dm^{-3} (KCl)) and 4.1 × 10^{-2} mol dm^{-3} (Birk and Logan,[5] I = 0.50 mol dm^{-3} (LiCl)). The values of K_a deduced from our data for the reactions of Ti(III) with $Co(phen)_3^{3+}$ and $Fe(phen)_3^{3+}$ ((1.5 ± 0.3) × 10^{-3} mol dm^{-3} and (4.3 ± 0.6) × 10^{-2} mol dm^{-3}, respectively) are within the range[5,16] of values deduced by previous workers. These values can therefore be reasonably accounted for in terms of the hydrolysis of Ti^{3+} (eq 5).

The reactions of Ti(III) with $Co(phen)_3^{3+}$ and $Fe(phen)_3^{3+}$ must be outer sphere since there are no available sites for inner-sphere precursor complex formation in these complexes. This is consistent with the accelerating effects of added anions

Table II. Dependence of k_{obsd} on Added Anions for the Ti(III) Reduction of $Co(phen)_3^{3+}$, $Co(C_2O_4)_3^{3-}$, and $Fe(phen)_3^{3+}$, at 25 °C, $I = 1.00$ mol dm^{-3} ($LiCl/LiClO_4$), $[H^+] = 0.10$ mol dm^{-3}

$Co(phen)_3^{3+}$

$[Co(phen)_3^{3+}] = 2.00 \times 10^{-5}$ mol dm^{-3}; $[Ti(III)] = 2.59 \times 10^{-3}$ mol dm^{-3}

$[Cl^-]$, mol dm^{-3}	k_{obsd}, dm^3 mol^{-1} s^{-1}	$[Cl^-]$, mol dm^{-3}	k_{obsd}, dm^3 mol^{-1} s^{-1}
0.11	2.57	0.80	2.63
0.20	2.58	1.00	2.65
0.55	2.60		

$Co(C_2O_4)_3^{3-}$

$[Co(C_2O_4)_3^{3-}] = 3.17 \times 10^{-4}$ mol dm^{-3}; $[Ti(III)] = 6.67 \times 10^{-3}$ mol dm^{-3}

$[Cl^-]$, mol dm^{-3}	$10^{-3}k_{obsd}$, dm^3 mol^{-1} s^{-1}	$[Cl^-]$, mol dm^{-3}	$10^{-3}k_{obsd}$, dm^3 mol^{-1} s^{-1}
0.05	0.81	0.60	0.76
0.20	0.75	0.80	0.75
0.40	0.79	1.00	0.81

$Fe(phen)_3^{3+}$

$[Fe(phen)_3^{3+}] = 2.0 \times 10^{-5}$ mol dm^{-3}; $[Ti(III)] = 5.7 \times 10^{-4}$ mol dm^{-3}

$[Cl^-]$, mol dm^{-3}	$10^{-5}k_{obsd}$, dm^3 mol^{-1} s^{-1}	$[Cl^-]$, mol dm^{-3}	$10^{-5}k_{obsd}$, dm^3 mol^{-1} s^{-1}
0.02	1.3	0.40	2.5
0.04	1.4	0.50	2.6
0.06	1.4	0.60	2.7
0.10	2.3	0.80	2.8
0.20	2.4		

$[Br^-]$, mol dm^{-3}	$10^{-5}k_{obsd}$, dm^3 mol^{-1} s^{-1}	$[Br^-]$, mol dm^{-3}	$10^{-5}k_{obsd}$, dm^3 mol^{-1} s^{-1}
0.02	2.8	0.40	5.7
0.04	2.9	0.50	6.0
0.06	3.7	0.70	6.8
0.10	4.0	0.80	7.2
0.20	4.2		

(Table II) as has been observed in other outer-sphere[12,17] redox reactions.

A direct calculation of the rate constant (k_1) for the reaction of $TiOH^{2+}$ with $Co(phen)_3^{3+}$ based on the Marcus equation[17] could not be made, because $E°$ for the $TiOH^{2+}/TiOH^{3+}$ couple is not known. In fact, there is no experimental evidence yet, establishing the existence of $TiOH^{3+}$ in aqueous solution. The equation[17]

$$k_{obsd} = k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \tag{7}$$

was, however, used to calculate the relative rate constant (k_1'/k_1) for the reactions of $TiOH^{2+}$ with $Co(bpy)_3^{3+}$ and $Co(phen)_3^{3+}$, respectively (where k_{11} is the exchange rate constant for the reductant, $TiOH^{2+}$ in this case, k_{22} is the exchange rate constant[12] for the oxidant, $Co(bpy)_3^{3+}$ (or $Co(phen)_3^{3+}$), K_{12} is the equilibrium constant[12] for the $TiOH^{2+}$ + $Co(bpy)_3^{3+}$ (or $Co(phen)_3^{3+}$) reaction and

$$\log f = \frac{(\log K_{12})^2}{4 \log (k_{11}k_{22}/z^2)}$$

where z is a frequency factor usually taken as 10^{11} dm^3 mol^{-1} s^{-1}). Since our data indicate that k_0 makes negligible contribution to k_{obsd} (eq 3 and the values of k_0 and k_1 obtained), as with the reactions of Thompson and Sykes,[4] we assumed that

$$k_{obsd} \approx k_1[H^+]^{-1} = k_{12} \tag{8}$$

therefore

$$(k_{12}'/k_{12})_{calcd} = (k_1'/k_1)_{calcd} \tag{9}$$

Table III. Values of k_3 and k_4/k_{-3} for Some Redox Systems

Reaction	k_3, dm^3 mol^{-1} s^{-1}	k_4/k_{-3}, mol dm^{-3}	Ref
Ti(III) + $Co(NH_3)_5N_3^{2+}$	47^a	0.045	1
Ti(III) + $Co(NH_3)_5SCN^{2+}$	495^b	0.026	2
Ti(III) + $Co(NH_3)_5F^{2+}$	562^a	0.112	4
Ti(III) + $Co(C_2O_4)_3^{3-}$	$1.89 \times 10^{3\,b}$	0.102	This work

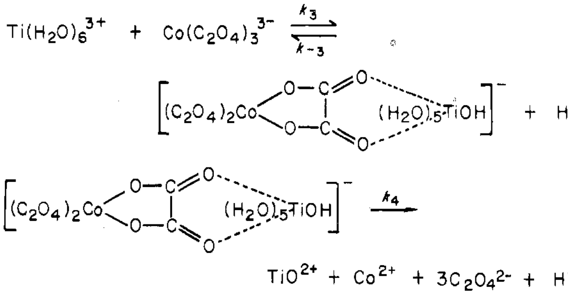
[a] $I = 0.50$ mol dm^{-3} (LiCl). [b] $I = 1.00$ mol dm^{-3} (LiCl).

The calculated value of (k_1'/k_1) is 0.20. From the results of Thompson and Sykes[4] on the outer-sphere redox reactions of $TiOH^{2+}$ with $Co(bpy)_3^{3+}$ ($k_1' = 4.4 \times 10^{-2}$ s^{-1}) and our results for the redox reactions of $TiOH^{2+}$ with $Co(phen)_3^{3+}$ ($k_1 = 0.25$ s^{-1})

$$(k_1'/k_1)_{expt} = 0.18$$

This is in excellent agreement with the calculated ratio, thus lending further support for the assignment of the outer-sphere mechanism to the reactions of $TiOH^{2+}$ with $Co(phen)_3^{3+}$.

Earlier studies on the redox reactions,[18,19] redox decomposition,[13,20] and racemization[21] of $Co(C_2O_4)_3^{3-}$ have given no indication of extensive protonation of $Co(C_2O_4)_3^{3-}$. We are not aware of any previously measured protonation constant for $Co(C_2O_4)_3^{3-}$. There are no strong reasons therefore for supposing that in the Ti(III) reduction of $Co(C_2O_4)_3^{3-}$, the acid dissociation of protonated tris(oxalato)cobaltate(III) is important in eq 6. The redox decomposition[13,20] of an aqueous solution of $Co(C_2O_4)_3^{3-}$ occurs with a rate constant that is negligible compared with the observed rate constant for the reaction of $TiOH^{2+}$ with $Co(C_2O_4)_3^{3-}$ in this study. Acid dissociation of Ti(III) alone cannot account for the large K (0.102 ± 0.012 mol dm^{-3}) obtained. We therefore suggest that the acid dependence of k_{obsd} as in eq 6[2,4] for $Co(C_2O_4)_3^{3-}$ indicates a series of reaction paths involving the equilibrium shown in eq 5 and the formation of a binuclear complex (eq 10) which is a precursor to the electron-transfer step (eq 11).



(10)

(11)

Application of the steady-state approximation to the concentration of the intermediate gives eq 12 which is of the same

$$k_{obsd} = k_3k_4/(k_{-3}[H^+] + k_4) \tag{12}$$

form as eq 6 with $a = 1/k_3$ and $b = k_{-3}/k_3k_4$. The values of a and b obtained for $Co(C_2O_4)_3^{3-}$ give k_3 as (1.89 ± 0.11) × 10^3 dm^3 mol^{-1} s^{-1} and k_4/k_{-3} as 0.102 mol dm^{-3}. Table III shows the values of k_3 and k_4/k_{-3} that have been obtained for some various redox systems for which precursor complex formation has been proposed. Our results are consistent with those of previous workers and hence the reactions of Ti(III) with $Co(C_2O_4)_3^{3-}$ are suggested to occur by an inner-sphere mechanism. Studies have indicated a rate constant for substitution[1] on Ti(III) as (2–4) × 10^3 dm^3 mol^{-1} s^{-1} and so the value of k_3 we obtain here is certainly consistent with a Ti(III) substitution-controlled process. The substitution-controlled process is facilitated[3a,22] by the fact that the oxalate ligand in $Co(C_2O_4)_3^{3-}$ is a strongly chelating moiety as can be noted in eq 10. Martin and Gould[3a] have reported the observed rate constant for the reduction of oxalatopentaamminecobalt(III) by Ti(III) at 25 °C, $I = 1.00$ mol dm^{-3}

(LiOTs), and $[H^+] = 0.10$ mol dm^{-3} as 1.2×10^2 dm^3 mol^{-1} s^{-1}. The observed value for $Co(C_2O_4)_3^{3-}$ under the same conditions in the present study is 8.0×10^2 dm^3 mol^{-1} s^{-1}, Table I. The enhanced reactivity of $Co(C_2O_4)_3^{3-}$ compared with $Co(NH_3)_5C_2O_4^+$ is probably due to the fact that $Co(C_2O_4)_3^{3-}$ forms a more stable precursor complex than does the positively charged $Co(NH_3)_5(C_2O_4)^+$ complex.

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Registry No. Ti(III), 22541-75-9; $Co(phen)_3^{3+}$, 18581-79-8; $Co(C_2O_4)_3^{3-}$, 15053-34-6; $Fe(phen)_3^{3+}$, 13479-49-7; Cl^-, 16887-00-6; Br^-, 24959-67-9.

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Contribution from the Institut für Anorganische Chemie,
Technische Universität Hannover, D 3000 Hannover, Federal Republic of Germany

Isomeric Pyrimidinecarboxylic Acids as Electron-Mediating Bridging Ligands in the Inner-Sphere Reduction of Cobalt(III) by Chromium(II)

H. BERTRAM, E. BÖLSING, H. SPIECKER, and K. WIEGHARDT*

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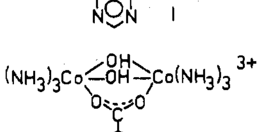
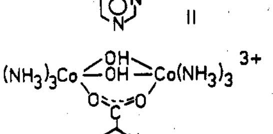
The kinetics of the Cr(II) reductions of two binuclear cobalt(III)–ammine complexes containing the isomeric 4- and 5-pyrimidinecarboxylate bridging ligands (I, II) in acidic perchlorate media have been studied. Inner-sphere mechanisms with attack of Cr(II) at a remote ring nitrogen and subsequent electron transfer through the organic ligands are assigned. Since the N-protonated forms of I and II react more rapidly, a radical-ion mechanism is proposed to be operative in both cases, although no direct evidence for the intervention of radical species was obtained. Due to steric hinderance by methyl groups, outer-sphere mechanisms are observed for the Cr(II) and V(II) reductions of the binuclear complex μ-4,6-dimethylpyrimidine-2-carboxylato(*O,O′*)-di-μ-hydroxo-bis[triamminecobalt(III)] and the μ-6-methylpyridine-2-carboxylato(*O,O′*) analogue (complexes III and IV).

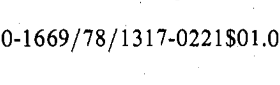
Introduction

In a previous paper, we reported the spectrophotometric detection of a reactive, strongly absorbing intermediate in the reduction of μ-pyrazinecarboxylato(*O,O′*)-di-μ-hydroxo-bis[triamminecobalt(III)] by chromium(II).[1] It was concluded that a coordinated radical is generated during the course of the reduction and that this decays intramolecularly. Due to the intrinsic reducibility of the aromatic, N-heterocyclic ligand, the persistence of the coordinated radical enabled the buildup of detectable concentrations of this species. In the present work we have studied the electron-mediating properties of isomeric pyrimidinecarboxylic acids. The aromatic, heterocyclic acids are easily reduced by chromium(II), probably because of the reduced π-electron density caused by the presence of two electronegative nitrogen atoms in the ring. It was therefore hoped to find further evidence for the occurrence of the "two-step" reduction mechanism when pyrimidinecarboxylic acids function as electron mediating bridges in the inner-sphere reduction of complexes I–IV by chromium(II).


I


II


III


IV

Experimental Section

Complexes and Reagents. The N-heterocyclic ligands were prepared by methods described in the literature: pyrimidine-4-carboxylic acid[2] and pyrimidine-5-carboxylic acid[3] were prepared from the corresponding methylpyrimidines by oxidation with $KMnO_4$ and, likewise, 4,6-dimethylpyrimidine-2-carboxylic acid was prepared from 2-hydroxophenyl-4,6-dimethylpyrimidine[4] and 6-methylpyridine-2-carboxylic acid from lutidine.[5]

The binuclear complexes I–IV were prepared from tri-μ-hydroxo-bis[triamminecobalt(III)] perchlorate in aqueous perchloric acid (0.5 M) following procedures described previously.[6] N-Protonated forms of complexes I–IV were isolated as perchlorate salts. Analytical data are summarized in Table I. The UV–visible spectra of all complexes are very similar (λ_{max} 524 nm, ϵ 110 ± 3 L mol^{-1} cm^{-1}). The presence of a symmetrical carboxylate bridge has been confirmed by an x-ray analysis of μ-pyrimidine-5-carboxylato-di-μ-hydroxo-bis[triamminecobalt(III)] perchlorate.[7]

Solutions of $[Cr(H_2O)_6]^{2+}$ and $[V(H_2O)_6]^{2+}$ in perchloric acid were prepared electrolytically as described previously.[1] Lithium perchlorate was obtained from Li_2CO_3 and concentrated $HClO_4$ and was recrystallized twice.

Physical Measurements. Kinetic runs were followed on a UNICAM SP 1700 spectrophotometer at the first absorption maximum of complexes I, III, and IV (λ_{max} 524 nm). Faster runs of the reactions of complexes I and II were followed on a Durrum stopped-flow spectrophotometer. Pseudo-first-order rate constants were obtained from the gradients (×2.303) of plots of log $(A_t - A_\infty)$ vs. time where A_t is the absorbance at time t and A_∞ that after 4–5 half-lives. Such plots were linear to better than 95% completion in all cases.

A protonation constant, K_1 (M^{-1}), was determined spectrophotometrically (λ 285 nm) at 1.0 M ionic strength ($LiClO_4$) for complex I. The value of $K_1 = 13.7 \pm 0.6$ M^{-1} was found to be independent of the temperature (10–41 °C) within experimental error. Complex