Kinetics and Mechanism of the Reductions of Tris(oxalato)cobaltate(III) Ion by Ruthenium(II) Species in Aqueous Solution

Josephine O. Ehighaokhuo, J. Folorunso Ojo, and Olusegun Olubuyide *

Department of Chemistry, University of Ife, Ile-Ife, Nigeria

The kinetics and mechanism of the reductions of $[Co(C_2O_4)_3]^{3-}$ by the ruthenium(II) species $[Ru(NH_3)_6]^{2+}$, $[Ru(en)_3]^{2+}$ (en = ethylenediamine), and $[Ru(NH_3)_5(H_2O)]^{2+}$ in aqueous solution have been investigated at $I = 0.20$ mol dm^{-3}(LiCl). The reductions are acid-independent in the range $[H^+] = 0.01$—0.10 mol dm^{-3}, and the second-order rate constants for the reductions at 25 °C are $(17.8 \pm 1.6) \times 10^{-2}$, $(5.5 \pm 0.3) \times 10^{-2}$, and $(3.3 \pm 0.3) \times 10^{-2}$ dm^3 mol^{-1} s^{-1} respectively. The activation parameters for the reductions by $[Ru(NH_3)_6]^{2+}$ and $[Ru(NH_3)_5(H_2O)]^{2+}$ are $\Delta H^{\ddagger} = 45.4 \pm 6.9$ kJ mol^{-1}, $\Delta S^{\ddagger} = -(107.6 \pm 22.9)$ J K^{-1} mol^{-1} and $\Delta H^{\ddagger} = 98.4 \pm 7.6$ kJ mol^{-1}, $\Delta S^{\ddagger} = +(56.5 \pm 4.2)$ J K^{-1} mol^{-1} respectively. The reductions by $[Ru(NH_3)_6]^{2+}$ and $[Ru(en)_3]^{2+}$ occur by an outer-sphere mechanism, while that by $[Ru(NH_3)_5(H_2O)]^{2+}$ occurs by a substitution-controlled inner-sphere mechanism.

The electron-mediating efficiency of the oxalate ligand between two transition-metal-ion centres in a transition state has been frequently used to demonstrate the existence of an inner-sphere mechanism in the reduction of oxalato-complexes of cobalt(III)[1—4] and ruthenium(III)[5] by the aqua-ions $[Fe(H_2O)_6]^{2+}$, $[V(H_2O)_6]^{2+}$, $[Cr(H_2O)_6]^{2+}$, and $[Ti(H_2O)_6]^{3+}$. While a direct product-identification criterion[1—3] has been used to establish this for the reductions by the first three reductants above, an indirect criterion[4,5] based on substitution-controlled rates was used for the reductions by $[Ti(H_2O)_6]^{3+}$.

Although $[Ru(NH_3)_5(H_2O)]^{2+}$ is a milder and less substitution-labile reductant than those above, its behaviour towards the oxalato-complexes of cobalt(III) and ruthenium(III) is worth investigating, taking into consideration the electron-mediating efficiency of oxalate ligand in its bidentate form. We earlier demonstrated[6] that $[Co(NH_3)_5(C_2O_4)]^+$ and $[Co(NH_3)_4(C_2O_4)]^+$ (in which the oxalate behaves as a uni- and bi-dentate ligand respectively) are reduced by $[Ru(NH_3)_5(H_2O)]^{2+}$ *via* an outer-sphere mechanism. The investigation reported here concerns $[Co(C_2O_4)_3]^{3-}$, a negative ion in which all the oxalate ligands are bidentate. Moreover, $[Ru(C_2O_4)_3]^{3-}$ is not reduced by $[Ru(NH_3)_5(H_2O)]^{2+}$ {E for $[Ru(C_2O_4)_3]^{3-/4-}$ couple[7] is -0.80 V *vs.* normal hydrogen electrode (n.h.e.)}, but $[Co(C_2O_4)_3]^{3-}$ is thermodynamically reducible by $[Ru(NH_3)_5(H_2O)]^{2+}$ {E for $[Co(C_2O_4)_3]^{3-/4-}$ is $+0.57$ V *vs.* n.h.e.[8]}. In this investigation the standard reference inert and outer-sphere reductants $[Ru(NH_3)_6]^{2+}$ and $[Ru(en)_3]^{2+}$ (en = ethylenediamine) have been included for comparison, as usual.

Experimental

Materials.—Commercial $[Ru(NH_3)_6]Cl_3$ (Johnson Matthey Ltd.) was recrystallised as described in the literature.[9] The salt $[Ru(NH_3)_5Cl]Cl_2$ was prepared and purified[9] from recrystallised $[Ru(NH_3)_6]Cl_3$, and $[Ru(en)_3]^{3+}$ was prepared as its tetrachlorozincate salt.[9] The ions $[Ru(NH_3)_6]^{2+}$, $[Ru(en)_3]^{2+}$, and $[Ru(NH_3)_5(H_2O)]^{2+}$ were generated from the above ruthenium(III) complexes by zinc analgam reduction[9] in an argon atmosphere. Tris(oxalato)cobaltate(III), $[Co(C_2O_4)_3]^{3-}$, was prepared and purified[4] as its potassium salt, the purity being confirmed by the u.v.–visible absorption spectrum ($\lambda_{max.} = 605$ nm, $\varepsilon = 175$ dm^3 mol^{-1} cm^{-1}).[4] This cobalt(III) complex is light-sensitive and so the dark bottle-green needle-shaped crystals of $K_3[Co(C_2O_4)_3]\cdot 3H_2O$ were kept in a tube wrapped in aluminium foil, to avoid photolysis. Lithium chloride (Hopkins and Williams reagent grade) was recrystallised twice, and HCl was AnalaR grade.

Kinetics.—All the reactions were followed on a Pye-Unicam u.v.–visible spectrophotometer (SP500) equipped with a direct read-out absorbance recorder. Reductions by $[Ru(en)_3]^{2+}$ and $[Ru(NH_3)_6]^{2+}$ were followed at the peak absorbance wavelengths[9] of the ruthenium(II) species, with cobalt(III) concentrations in at least 10-fold excess over the ruthenium(II) concentrations. The reductions by $[Ru(NH_3)_5(H_2O)]^{2+}$ were followed under pseudo-first-order conditions too, at either $\lambda = 605$ nm, the peak[4] absorbance wavelength for $[Co(C_2O_4)_3]^{3-}$ ($\varepsilon = 175$ dm^3 mol^{-1} cm^{-1}), or $\lambda = 300$ nm, the peak absorbance wavelength for $[Ru(NH_3)_5(H_2O)]^{2+}$ ($\varepsilon = 1.18 \times 10^3$ dm^3 mol^{-1} cm^{-1}).[9] The rate constants measured were consistent and independent of wavelength. The cell compartment was thermostatted to the desired temperature within ±0.1 °C.

Results

The stoicheiometry of each reaction was checked by measuring the ruthenium(II) consumed at its u.v. absorption peak under conditions of a two- to three-fold excess of the ruthenium(II) reductant over the cobalt(III) oxidant. All the results conform to the general equation (1). Pseudo-first-order rate plots were obtained for more than four half-lives in all cases, and the second-order rate constants derived from these were consistent with the rate law (2).

$$Ru^{II} + Co^{III} \longrightarrow Ru^{III} + Co^{II} \qquad (1)$$

$$-d[Co^{III}]/dt = -d[Ru^{II}]/dt = k_{obs.}[Co^{III}][Ru^{II}] \qquad (2)$$

All the reactions are acid-independent over the range $[H^+] = 0.01$—0.10 mol dm^{-3}, and at 25 °C, $I = 0.20$ mol dm^{-3}(LiCl) the observed second-order rate constants k_2 are $(17.8 \pm 1.6) \times 10^{-2}$, $(5.5 \pm 0.3) \times 10^{-2}$, and $(3.3 \pm 0.3) \times 10^{-2}$ dm^3 mol^{-1} s^{-1} for reductions by $[Ru(NH_3)_6]^{2+}$, $[Ru(en)_3]^{2+}$, and $[Ru(NH_3)_5(H_2O)]^{2+}$ respectively (Table 1). From the variation of the second-order constants with temperature (Table 2), the activation parameters were calculated using the least-squares method; for the reductions by $[Ru(NH_3)_6]^{2+}$ and $[Ru(NH_3)_5(H_2O)]^{2+}$ the values are $\Delta H^{\ddagger} = 45.4 \pm 6.9$ kJ

Table 1. Second-order rate constants* for the reductions of $[Co(C_2O_4)_3]^{3-}$ by ruthenium(II) species at 25 °C and I = 0.20 mol dm^{-3} *(LiCl)*

(*a*) $[Ru(en)_3]^{2+}$
$\{[Co^{III}] = (1.0—2.0) \times 10^{-3}, [Ru^{II}] = 1.0 \times 10^{-4}$ mol dm$^{-3}\}$

$[H^+]$/mol dm^{-3}	10^2k_2/dm^3 mol^{-1} s^{-1}
0.10	5.5
0.05	5.4
0.03	5.2
0.02	5.8

(*b*) $[Ru(NH_3)_6]^{2+}$
$\{[Co^{III}] = (1.0—3.5) \times 10^{-3}, [Ru^{II}] = (1.0—2.0) \times 10^{-4}$ mol dm$^{-3}\}$

$[H^+]$/mol dm^{-3}	10^2k_2/dm^3 mol^{-1} s^{-1}
0.10	17.0
0.05	18.2
0.05	17.4
0.02	18.7

(*c*) $[Ru(NH_3)_5(H_2O)]^{2+}$
$\{[Co^{III}] = (0.2—4.4) \times 10^{-3}, [Ru^{II}] = (1.0—20.0) \times 10^{-4}$ mol dm$^{-3}\}$

$[H^+]$/mol dm^{-3}	10^2k_2/dm^3 mol^{-1} s^{-1}
0.10	3.4
0.05	3.8
0.04	3.1
0.02	3.2
0.01	3.0

* k_2 at $[H^+]$ = 0.10 mol dm^{-3} for each reductant is the average from at least five runs at various reductant and oxidant concentrations. At other acid concentrations k_2 is the average from two to three runs.

Table 2. Temperature dependence of the second-order rate constants* for the reductions of $[Co(C_2O_4)_3]^{3-}$ by ruthenium(II) species, I = 0.20 mol dm^{-3} (LiCl)

(*a*) $[Ru(NH_3)_6]^{2+}$
$\{[Co^{III}] = (1.0—2.8) \times 10^{-3}, [Ru^{II}] = (1.0—2.5) \times 10^{-4}$ mol dm$^{-3}\}$

θ_c/°C	10^2k_2/dm^3 mol^{-1} s^{-1}
20.0	11.4
25.0	17.8
32.0	23.0
35.0	32.5

(*b*) $[Ru(NH_3)_5(H_2O)]^{2+}$
$\{[Co^{III}] = (0.2—4.4) \times 10^{-3}, [Ru^{II}] = (1.0—20.0) \times 10^{-4}$ mol dm$^{-3}\}$

θ_c/°C	10^2k_2/dm^3 mol^{-1} s^{-1}
20.0	1.7
25.0	3.3
30.0	6.1
35.0	15.0

* k_2 at 25 °C for each reductant is the average of values from Table 1. At other temperatures, k_2 is the average from at least three runs for each temperature.

Table 3. Exchange rate constants for some cobalt complexes

Complexes	k_{22}/dm^3 mol^{-1} s^{-1}	Ref.
$[Co(en)_3]^{3+/2+}$	2.0×10^{-5}	14
$[Co(C_2O_4)_3]^{3-/4-}$	1.4×10^{-12}	This work
$[Co(NH_3)_6]^{3+/2+}$	$\leqslant 1 \times 10^{-9}$	14
$[Co(phen)_3]^{3+/2+}$	5.0	14
$[Co(bipy)_3]^{3+/2+}$	7.0	14

mol^{-1}, $\Delta S^{\ddagger} = -(107.6 \pm 22.9)$ J K^{-1} mol^{-1} and 98.4 ± 7.6 kJ mol^{-1}, $+(56.5 \pm 4.2)$ J K^{-1} mol^{-1} respectively.

Discussion

Tris(oxalato)cobaltate(III) is reduced by $[Ru(NH_3)_6]^{2+}$ and $[Ru(en)_3]^{2+}$ by an outer-sphere mechanism, since the reductants lack co-ordination sites for inner-sphere complex formation. All the three oxalate ligands in $[Co(C_2O_4)_3]^{3-}$ are bidentate, with the two negative oxygen ends on each oxalate co-ordinated to cobalt(III), so that in the acid concentration range used in this study (0.01—0.10 mol dm^{-3}) protonation of $[Co(C_2O_4)_3]^{3-}$ is not expected to occur. Earlier studies using this oxidant at even higher $[H^+]$ gave no indication of extensive protonation.[4,10] It is not surprising therefore that, in this study, no acid dependence of the rate constants was observed. This is in contrast to an earlier study[6] using $[Co(NH_3)_5(C_2O_4)]^+$ (where the oxalate ligand is unidentate, with a free negative oxygen end) in which an acid dependence was observed.

An estimate[4,11] of the exchange rate constants k_{22} for the couple $[Co(C_2O_4)_3]^{3-/4-}$ was made from the Marcus cross relation (3) using an iterative procedure, where k_{11} is the

$$k_{obs.} = k_{12} = (k_{11}k_{22}K_{12}f)^{\frac{1}{2}} \qquad (3)$$

exchange rate constant for the reductant couple[12] $[Ru(NH_3)_6]^{2+/3+}$ ($k_{11} = 8.2 \times 10^2$ dm^3 mol^{-1} s^{-1}), $\log f = (\log K_{12})^2/4 \log (k_{11}k_{22}/Z^2)$, with $Z = 10^{11}$ dm^3 mol^{-1} s^{-1}, and K_{12} was calculated from the known redox potentials[8,13] for $[Co(C_2O_4)_3]^{3-/4-}$ and $[Ru(NH_3)_6]^{2+/3+}$. The result was $k_{22} = 1.4 \times 10^{-12}$ dm^3 mol^{-1} s^{-1}. This is a reasonable estimate, considering the values that have been estimated for other cobalt(III) complexes[14] of similar structure (Table 3), though the last two entries, $[Co(phen)_3]^{3+/2+}$ (phen = 1,10-phenanthroline) and $[Co(bipy)_3]^{3+/2+}$ (bipy = 2,2′-bipyridyl), are high, probably as a result of the π-delocalised electrons of the substituted aromatic ligands.

The rate constant for the reduction of $[Co(C_2O_4)_3]^{3-}$ by $[Ru(NH_3)_5(H_2O)]^{2+}$ at 25 °C, $(3.3 \pm 0.3) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}, lies in the range $[(ca.\ 2.6—30.0) \times 10^{-2}$ mol^{-1} s$^{-1}]$ characteristic of $[Ru(NH_3)_5(H_2O)]^{2+}$ substitutions. We also recently measured the rate constant for the substitution[15] of oxalate ligand in $[Ru(NH_3)_5(H_2O)]^{2+}$ at 25 °C and I = 0.20 mol dm^{-3} (LiCl) as 3.0×10^{-2} dm^3 mol^{-1} s^{-1}.

We suggest therefore that the redox reaction between $[Co(C_2O_4)_3]^{3-}$ and $[Ru(NH_3)_5(H_2O)]^{2+}$ occurs by a substitution-controlled inner-sphere mechanism. By similar reasoning, the redox reactions between this reductant and each of $[Co(NH_3)_5F]^{2+}$ and $[Co(NH_3)_5Cl]^{2+}$ have recently been classified[9] as inner-sphere. The negative charge on $[Co(C_2O_4)_3]^{3-}$ {relative to the positive charge on each of $[Co(NH_3)_5(C_2O_4)]^+$ and $[Co(NH_3)_4(C_2O_4)]^+$, oxidants which are reduced by this reductant by an outer-sphere mechanism[6]} facilitates coulombic attraction towards $[Ru(NH_3)_5(H_2O)]^{2+}$, leading to effective orbital overlap and bridge formation. This is reinforced in the transition state by the presence of the effective 'lead-in' oxalate ligand.

The complex $[Ru(NH_3)_5(C_2O_4)]^+$ was detected and subsequently isolated as the ruthenium(III) product of the reduction of $[Co(C_2O_4)_3]^{3-}$ by $[Ru(NH_3)_5(H_2O)]^{2+}$. It was characterised by its u.v. absorption spectrum ($\lambda_{max.}$ = 288 nm, ε = 2.98×10^3 dm^3 mol^{-1} cm^{-1}; lit.,[5] $\lambda_{max.}$ = 288 nm, ε = 3.09×10^3 dm^3 mol^{-1} cm^{-1}). This confirms an inner-sphere path for this reaction.

The enthalpy of activation for the reduction of $[Co(C_2O_4)_3]^{3-}$ by $[Ru(NH_3)_5(H_2O)]^{2+}$, 98.4 ± 7.6 kJ mol^{-1}, is of the same order of magnitude as those reported for substitutions on aquaruthenium(II) species.[16,17] This also confirms that the reduction of $[Co(C_2O_4)_3]^{3-}$ by $[Ru(NH_3)_5(H_2O)]^{2+}$ occurs by a substitution-controlled process. Furthermore, the positive entropy of activation, +(56.5 ± 4.2) J K^{-1} mol^{-1}, is of the same order of magnitude as those reported for SCN^- and $CH_3CO_2^-$ substitutions on penta-ammineaquaruthenium(II).[15]

The ion $[Ru(C_2O_4)_3]^{3-}$ is not reduced by $[Ru(NH_3)_5(H_2O)]^{2+}$ due to the unfavourable free-energy change. As pointed out previously,[9,11] the energy barrier imposed on cobalt(III) to bring about the transition $t_{2g}^6 \longrightarrow t_{2g}^6e^1$ is often partially overcome by the exothermic formation of a precursor complex and hence inner-sphere electron transfer. Such a barrier is not important in Ru^{III} ($t_{2g}^5 \longrightarrow t_{2g}^6$), and electron transfer easily occurs by an outer-sphere mechanism.

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