

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

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The kinetics and mechanism of the reductions of  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  by the ruthenium(II) species  $[\text{Ru}(\text{NH}_3)_6]^{2+}$ ,  $[\text{Ru}(\text{en})_3]^{2+}$  (en = ethylenediamine), and  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  in aqueous solution have been investigated at  $I = 0.20 \text{ mol dm}^{-3}(\text{LiCl})$ . The reductions are acid-independent in the range  $[\text{H}^+] = 0.01\text{--}0.10 \text{ mol dm}^{-3}$ , and the second-order rate constants for the reductions at  $25^\circ\text{C}$  are  $(17.8 \pm 1.6) \times 10^{-2}$ ,  $(5.5 \pm 0.3) \times 10^{-2}$ , and  $(3.3 \pm 0.3) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  respectively. The activation parameters for the reductions by  $[\text{Ru}(\text{NH}_3)_6]^{2+}$  and  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  are  $\Delta H^\ddagger = 45.4 \pm 6.9 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -(107.6 \pm 22.9) \text{ J K}^{-1} \text{ mol}^{-1}$  and  $\Delta H^\ddagger = 98.4 \pm 7.6 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = +(56.5 \pm 4.2) \text{ J K}^{-1} \text{ mol}^{-1}$  respectively. The reductions by  $[\text{Ru}(\text{NH}_3)_6]^{2+}$  and  $[\text{Ru}(\text{en})_3]^{2+}$  occur by an outer-sphere mechanism, while that by  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  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)<sup>1-4</sup> and ruthenium(III)<sup>5</sup> by the aqua-ions  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{V}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ , and  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ . While a direct product-identification criterion<sup>1-3</sup> has been used to establish this for the reductions by the first three reductants above, an indirect criterion<sup>4,5</sup> based on substitution-controlled rates was used for the reductions by  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ .

Although  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  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<sup>6</sup> that  $[\text{Co}(\text{NH}_3)_5(\text{C}_2\text{O}_4)]^+$  and  $[\text{Co}(\text{NH}_3)_4(\text{C}_2\text{O}_4)]^+$  (in which the oxalate behaves as a uni- and bi-dentate ligand respectively) are reduced by  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  via an outer-sphere mechanism. The investigation reported here concerns  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ , a negative ion in which all the oxalate ligands are bidentate. Moreover,  $[\text{Ru}(\text{C}_2\text{O}_4)_3]^{3-}$  is not reduced by  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  { $E$  for  $[\text{Ru}(\text{C}_2\text{O}_4)_3]^{3-/4-}$  couple<sup>7</sup> is  $-0.80 \text{ V vs. normal hydrogen electrode (n.h.e.)}$ }, but  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  is thermodynamically reducible by  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  { $E$  for  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-/4-}$  is  $+0.57 \text{ V vs. n.h.e.}$ <sup>8</sup>}. In this investigation the standard reference inert and outer-sphere reductants  $[\text{Ru}(\text{NH}_3)_6]^{2+}$  and  $[\text{Ru}(\text{en})_3]^{2+}$  (en = ethylenediamine) have been included for comparison, as usual.

### Experimental

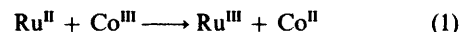
**Materials.**—Commercial  $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$  (Johnson Matthey Ltd.) was recrystallised as described in the literature.<sup>9</sup> The salt  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  was prepared and purified<sup>9</sup> from recrystallised  $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ , and  $[\text{Ru}(\text{en})_3]^{3+}$  was prepared as its tetrachlorozincate salt.<sup>9</sup> The ions  $[\text{Ru}(\text{NH}_3)_6]^{2+}$ ,  $[\text{Ru}(\text{en})_3]^{2+}$ , and  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  were generated from the above ruthenium(III) complexes by zinc amalgam reduction<sup>9</sup> in an argon atmosphere. Tris(oxalato)cobaltate(III),  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ , was prepared and purified<sup>4</sup> as its potassium salt, the purity being confirmed by the u.v.-visible absorption spectrum ( $\lambda_{\text{max.}} = 605 \text{ nm}$ ,  $\epsilon = 175 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ).<sup>4</sup> This cobalt(III) complex is light-sensitive and so the dark bottle-green needle-shaped crystals of  $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$  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  $[\text{Ru}(\text{en})_3]^{2+}$  and  $[\text{Ru}(\text{NH}_3)_6]^{2+}$  were followed at the peak absorbance wavelengths<sup>9</sup> of the ruthenium(II) species, with cobalt(III) concentrations in at least 10-fold excess over the ruthenium(II) concentrations. The reductions by  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  were followed under pseudo-first-order conditions too, at either  $\lambda = 605 \text{ nm}$ , the peak<sup>4</sup> absorbance wavelength for  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  ( $\epsilon = 175 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ), or  $\lambda = 300 \text{ nm}$ , the peak absorbance wavelength for  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  ( $\epsilon = 1.18 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ).<sup>9</sup> The rate constants measured were consistent and independent of wavelength. The cell compartment was thermostatted to the desired temperature within  $\pm 0.1^\circ\text{C}$ .

### Results

The stoichiometry 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).

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

All the reactions are acid-independent over the range  $[\text{H}^+] = 0.01\text{--}0.10 \text{ mol dm}^{-3}$ , and at  $25^\circ\text{C}$ ,  $I = 0.20 \text{ mol dm}^{-3}(\text{LiCl})$  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  $(3.3 \pm 0.3) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for reductions by  $[\text{Ru}(\text{NH}_3)_6]^{2+}$ ,  $[\text{Ru}(\text{en})_3]^{2+}$ , and  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  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  $[\text{Ru}(\text{NH}_3)_6]^{2+}$  and  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  the values are  $\Delta H^\ddagger = 45.4 \pm 6.9 \text{ kJ}$

**Table 1.** Second-order rate constants\* for the reductions of  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  by ruthenium(II) species at 25 °C and  $I = 0.20 \text{ mol dm}^{-3}$  (LiCl)

(a) $[\text{Ru}(\text{en})_3]^{2+}$ $\{[\text{Co}^{\text{III}}] = (1.0\text{--}2.0) \times 10^{-3}, [\text{Ru}^{\text{II}}] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}\}$		
$[\text{H}^+]/\text{mol dm}^{-3}$	$10^2 k_2/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	
0.10	5.5	
0.05	5.4	
0.03	5.2	
0.02	5.8	
(b) $[\text{Ru}(\text{NH}_3)_6]^{2+}$ $\{[\text{Co}^{\text{III}}] = (1.0\text{--}3.5) \times 10^{-3}, [\text{Ru}^{\text{II}}] = (1.0\text{--}2.0) \times 10^{-4} \text{ mol dm}^{-3}\}$		
0.10	17.0	
0.05	18.2	
0.05	17.4	
0.02	18.7	
(c) $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$ $\{[\text{Co}^{\text{III}}] = (0.2\text{--}4.4) \times 10^{-3}, [\text{Ru}^{\text{II}}] = (1.0\text{--}20.0) \times 10^{-4} \text{ mol dm}^{-3}\}$		
0.10	3.4	
0.05	3.8	
0.04	3.1	
0.02	3.2	
0.01	3.0	

\*  $k_2$  at  $[\text{H}^+] = 0.10 \text{ mol dm}^{-3}$  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  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  by ruthenium(II) species,  $I = 0.20 \text{ mol dm}^{-3}$  (LiCl)

(a) $[\text{Ru}(\text{NH}_3)_6]^{2+}$ $\{[\text{Co}^{\text{III}}] = (1.0\text{--}2.8) \times 10^{-3}, [\text{Ru}^{\text{II}}] = (1.0\text{--}2.5) \times 10^{-4} \text{ mol dm}^{-3}\}$		
$\theta_c/\text{°C}$	$10^2 k_2/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	
20.0	11.4	
25.0	17.8	
32.0	23.0	
35.0	32.5	
(b) $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$ $\{[\text{Co}^{\text{III}}] = (0.2\text{--}4.4) \times 10^{-3}, [\text{Ru}^{\text{II}}] = (1.0\text{--}20.0) \times 10^{-4} \text{ mol dm}^{-3}\}$		
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.

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

## Discussion

Tris(oxalato)cobaltate(III) is reduced by  $[\text{Ru}(\text{NH}_3)_6]^{2+}$  and  $[\text{Ru}(\text{en})_3]^{2+}$  by an outer-sphere mechanism, since the reductants lack co-ordination sites for inner-sphere complex formation. All the three oxalate ligands in  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  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  $\text{mol dm}^{-3}$ ) protonation of  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  is not expected to occur. Earlier studies using this oxidant at even higher  $[\text{H}^+]$  gave no indication of extensive

**Table 3.** Exchange rate constants for some cobalt complexes

Complexes	$k_{22}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	Ref.
$[\text{Co}(\text{en})_3]^{3+/2+}$	$2.0 \times 10^{-5}$	14
$[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-/4-}$	$1.4 \times 10^{-12}$	This work
$[\text{Co}(\text{NH}_3)_6]^{3+/2+}$	$\leq 1 \times 10^{-9}$	14
$[\text{Co}(\text{phen})_3]^{3+/2+}$	5.0	14
$[\text{Co}(\text{bipy})_3]^{3+/2+}$	7.0	14

protonation.<sup>4,10</sup> 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<sup>6</sup> using  $[\text{Co}(\text{NH}_3)_5(\text{C}_2\text{O}_4)]^+$  (where the oxalate ligand is unidentate, with a free negative oxygen end) in which an acid dependence was observed.

An estimate<sup>4,11</sup> of the exchange rate constants  $k_{22}$  for the couple  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-/4-}$  was made from the Marcus cross relation (3) using an iterative procedure, where  $k_{11}$  is the

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

exchange rate constant for the reductant couple<sup>12</sup>  $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$  ( $k_{11} = 8.2 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ),  $\log f = (\log K_{12})^2/4 \log(k_{11}k_{22}/Z^2)$ , with  $Z = 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , and  $K_{12}$  was calculated from the known redox potentials<sup>8,13</sup> for  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-/4-}$  and  $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ . The result was  $k_{22} = 1.4 \times 10^{-12} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . This is a reasonable estimate, considering the values that have been estimated for other cobalt(III) complexes<sup>14</sup> of similar structure (Table 3), though the last two entries,  $[\text{Co}(\text{phen})_3]^{3+/2+}$  (phen = 1,10-phenanthroline) and  $[\text{Co}(\text{bipy})_3]^{3+/2+}$  (bipy = 2,2'-bipyridyl), are high, probably as a result of the  $\pi$ -delocalised electrons of the substituted aromatic ligands.

The rate constant for the reduction of  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  by  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  at 25 °C,  $(3.3 \pm 0.3) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , lies in the range  $[ca. 2.6\text{--}30.0) \times 10^{-2} \text{ mol}^{-1} \text{ s}^{-1}]$  characteristic of  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  substitutions. We also recently measured the rate constant for the substitution<sup>15</sup> of oxalate ligand in  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  at 25 °C and  $I = 0.20 \text{ mol dm}^{-3}$  (LiCl) as  $3.0 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

We suggest therefore that the redox reaction between  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  and  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  occurs by a substitution-controlled inner-sphere mechanism. By similar reasoning, the redox reactions between this reductant and each of  $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$  and  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  have recently been classified<sup>9</sup> as inner-sphere. The negative charge on  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  (relative to the positive charge on each of  $[\text{Co}(\text{NH}_3)_5(\text{C}_2\text{O}_4)]^+$  and  $[\text{Co}(\text{NH}_3)_4(\text{C}_2\text{O}_4)]^+$ , oxidants which are reduced by this reductant by an outer-sphere mechanism<sup>6</sup>) facilitates coulombic attraction towards  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$ , 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  $[\text{Ru}(\text{NH}_3)_5(\text{C}_2\text{O}_4)]^+$  was detected and subsequently isolated as the ruthenium(III) product of the reduction of  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  by  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$ . It was characterised by its u.v. absorption spectrum ( $\lambda_{\text{max.}} = 288 \text{ nm}$ ,  $\epsilon = 2.98 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ; lit.<sup>5</sup>  $\lambda_{\text{max.}} = 288 \text{ nm}$ ,  $\epsilon = 3.09 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ). This confirms an inner-sphere path for this reaction.

The enthalpy of activation for the reduction of  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  by  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$ ,  $98.4 \pm 7.6 \text{ kJ mol}^{-1}$ , is of the same order of magnitude as those reported for substitutions on aquaruthenium(II) species.<sup>16,17</sup> This also confirms that the reduction of  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  by  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  occurs by a substitution-controlled process. Furthermore, the positive

entropy of activation,  $+(56.5 \pm 4.2) \text{ J K}^{-1} \text{ mol}^{-1}$ , is of the same order of magnitude as those reported for  $\text{SCN}^-$  and  $\text{CH}_3\text{-CO}_2^-$  substitutions on penta-ammineaquaruthenium(II).<sup>15</sup>

The ion  $[\text{Ru}(\text{C}_2\text{O}_4)_3]^{3-}$  is not reduced by  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  due to the unfavourable free-energy change. As pointed out previously,<sup>9,11</sup> the energy barrier imposed on cobalt(III) to bring about the transition  $t_{2g}^6 \longrightarrow t_{2g}^6 e^1$  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  $\text{Ru}^{\text{III}}$  ( $t_{2g}^5 \longrightarrow t_{2g}^6$ ), and electron transfer easily occurs by an outer-sphere mechanism.

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