Notes

Kinetics and Mechanism of the Oxidation of Ruthenium(II) Ammines by Tetra-ammine(oxalato)- and Penta-ammine(hydrogenoxalato)-cobalt(III) Complexes

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The oxidations of $[Ru(NH_3)_6]^{2+}$ and $[Ru(NH_3)_5(OH_2)]^{2+}$ by $[Co(NH_3)_4(C_2O_4)]^+$ and $[Co(NH_3)_5(HC_2O_4)]^{2+}$ have been investigated at an ionic strength of 0.20 mol dm^{-3} (LiCl) at various acid (HCl) concentrations. The oxidation of both ruthenium(II) species by $[Co(NH_3)_4(C_2O_4)]^+$ is acid-independent whereas that by $[Co(NH_3)_5(HC_2O_4)]^{2+}$ is acid-inhibited. The activation parameters $\Delta H^\ddagger$ (kJ mol^{-1}) and $\Delta S^\ddagger$ (J K^{-1} mol^{-1}) for the reactions of $[Co(NH_3)_4(C_2O_4)]^+$ with $[Ru(NH_3)_6]^{2+}$ and $[Ru(NH_3)_5(OH_2)]^{2+}$ are respectively: 60.5 ± 5.9, −24.6 ± 3.1; 66.3 + 6.1, −11.9 ± 1.8. All the reactions studied occur by an outer-sphere mechanism.

IN the past, the redox chemistry of ruthenium(II) ammines has received considerable attention [1–7] due to the inertness of these complexes relative to other labile reductants, such as Cr^{II}, Eu^{II}, U^{III}, Ti^{III}, and V^{II}. In our laboratory, the continued interest in $[Ru(NH_3)_5(OH_2)]^{2+}$ in particular [7,8] lies in the greater lability of this complex relative to other ruthenium(II) species, such as $[Ru(NH_3)_6]^{2+}$ and $[Ru(en)_3]^{2+}$ (en = ethylenediamine).

The oxalate ion provides an efficient bridging mechanism [9–16] for the reduction of cobalt(III) and ruthenium(III) complexes by its chelating tendency. In a previous study,[8] however, we demonstrated that $[Ru(NH_3)_5(OH_2)]^{2+}$ reduces the oxalato-complexes of ruthenium(III) by an outer-sphere mechanism. The present study was, therefore, undertaken in order to determine whether $[Ru(NH_3)_5(OH_2)]^{2+}$ could reduce the cobalt(III) analogues by a bridging mechanism.

EXPERIMENTAL

Materials.—$[Ru(NH_3)_6]Cl_3$ (Johnson Matthey Ltd.) was recrystallised twice from hot 0.10 mol dm^{-3} HCl as described previously.[17] The complex $[Ru(NH_3)_5Cl]Cl_2$ was prepared from a pure sample of $[Ru(NH_3)_6]Cl_3$ as described in the literature.[17] Solutions of $[Ru(NH_3)_6]^{2+}$ and $[Ru(NH_3)_5(OH_2)]^{2+}$ were freshly prepared by the reduction of acidic solutions of pure $[Ru(NH_3)_6]Cl_3$ and $[Ru(NH_3)_5Cl]Cl_2$ using zinc amalgam in an atmosphere of oxygen-free argon.[7]

The complex $[Co(NH_3)_4(C_2O_4)]Cl$ was prepared and purified,[18] and characterised by means of its u.v.-visible absorption spectrum.[19–21] The complex $[Co(NH_3)_5(HC_2O_4)]Cl_2$ was prepared [12] and determined to be pure by analysis of the cobalt and oxalate (C_2O_4) contents [22,23] (Found: Co, 19.25; oxalate, 29.0. Calc. for $C_2H_{16}Cl_2CoN_5O_4$: Co, 19.4; oxalate, 28.95%).

Kinetics.—All the reactions were studied in LiCl–HCl media by conventional techniques using a thermostatted Pye–Unicam SP500 spectrophotometer regulated to the desired temperature. An atmosphere of pure argon and chloride media were employed since ruthenium(II) is sensitive to air and perchlorate ions.[5,7,8] A low ionic strength (0.20 mol dm^{-3}) was maintained throughout because of the limited solubility of ruthenium(II).[5,7,12] The oxidation of both ruthenium(II) species by $[Co(NH_3)_4(C_2O_4)]^+$ and the oxidation of $[Ru(NH_3)_5(OH_2)]^{2+}$ by $[Co(NH_3)_5(HC_2O_4)]^{2+}$ were studied under pseudo-first-order conditions. With $[Co(NH_3)_4(C_2O_4)]^+$ as oxidant, reactions were studied at $\lambda_{max.} = 505$ nm where $\varepsilon_{max.} = 71$ dm^3 mol^{-1} cm^{-1} for the oxidant,[19–21] while with $[Co(NH_3)_5(HC_2O_4)]^{2+}$ as oxidant, reactions were studied at $\lambda_{max.} = 300$ nm ($\varepsilon_{max.} = 1.18 \times 10^3$ dm^3 mol^{-1} cm^{-1}).

The oxidation of $[Ru(NH_3)_6]^{2+}$ by $[Co(NH_3)_5(HC_2O_4)]^{2+}$ was studied under proportional (equal initial concentrations of reactants) second-order conditions at the absorbance maximum of the reductant $[Ru(NH_3)_6]^{2+}$ ($\lambda_{max.} = 275$ nm, $\varepsilon_{max.} = 625$ dm^3 mol^{-1} cm^{-1}).[24] The integrated rate law used to analyse the data, which takes account of species possessing significant absorbance at the absorption peak of the reductant, is given by equation (1) where ε is the molar

$$(k_2/l\Delta\varepsilon)t = [A_0\varepsilon_{Ru^{III}}(\varepsilon_{Ru^{II}} + \varepsilon_{Co^{III}})^{-1} - A_t]^{-1} - [A_0\Delta\varepsilon(\varepsilon_{Ru^{II}} + \varepsilon_{Co^{III}})^{-1}]^{-1} \quad (1)$$

absorption coefficient of the given species at the wavelength of the kinetic measurement, A_0 is the total initial absorbance of the reactants, A_t is the total absorbance of the reaction mixture after time t (s), $\Delta\varepsilon = \varepsilon_{Ru^{III}} - (\varepsilon_{Ru^{II}} + \varepsilon_{Co^{III}})$, k_2 is the second-order rate constant (dm^3 mol^{-1} s^{-1}), and l is the pathlength (cm). The second-order rate plots were linear to at least four half-lives in all runs.

RESULTS

All the reactions conformed to 1 : 1 stoicheiometry, equation (2). Furthermore, the kinetic data fit rate law (3)

$$Co^{III} + Ru^{II} \longrightarrow Co^{II} + Ru^{III} \quad (2)$$

$$-d[Co^{III}]/dt = k_{obs.}[Co^{III}][Ru^{II}] \quad (3)$$

for various concentrations of the oxidant and reductant. For the oxidation of the two ruthenium(II) species by $[Co(NH_3)_4(C_2O_4)]^+$ at 25 °C and an ionic strength of 0.20 mol dm^{-3} (LiCl), $k_{obs.}$ values are independent of the acid concentration (Table 1). On the other hand, $k_{obs.}$ values for the oxidation of the two ruthenium(II) species by $[Co(NH_3)_5(HC_2O_4)]^{2+}$ decrease with increasing acid concentration in the range 0.01—0.04 mol dm^{-3} (HCl) at 25 °C and $I = 0.20$ mol dm^{-3} (LiCl) (Table 2). The observed acid dependence may be explained by the following reaction scheme, equations (4)—(6). The rate law obtained using this scheme is

$$[Co(NH_3)_5(HC_2O_4)]^{2+} \overset{K_a}{\rightleftharpoons} [Co(NH_3)_5(C_2O_4)]^+ + H^+ \quad (4)$$

$$[Co(NH_3)_5(C_2O_4)]^+ + Ru^{II} \xrightarrow{k_0} \text{products} \quad (5)$$

$$[Co(NH_3)_5(HC_2O_4)]^{2+} + Ru^{II} \xrightarrow{k_1} \text{products} \quad (6)$$

TABLE 1

Rate constants ($k_{obs.}$) [a] for the oxidation of $[Co(NH_3)_4(C_2O_4)]^+$ by $[Ru(NH_3)_6]^{2+}$ and $[Ru(NH_3)_5(OH_2)]^{2+}$, $I = 0.20$ mol dm^{-3} (LiCl)

$[Ru(NH_3)_5(OH_2)]^{2+}$ + $[Co(NH_3)_4(C_2O_4)]^+$ [b]			$[Ru(NH_3)_6]^{2+}$ + $[Co(NH_3)_4(C_2O_4)]^+$ [c]		
$[H^+]$/ mol dm^{-3}	θ_c/°C	$k_{obs.}$/dm^3 mol^{-1} s^{-1}	$[H^+]$/ mol dm^{-3}	θ_c/°C	$k_{obs.}$/dm^3 mol^{-1} s^{-1}
0.05	25	3.7	0.05	25	7.8
0.10	25	3.8	0.10	25	7.9
0.15	25	3.7	0.15	25	7.7
0.10	15	1.4	0.10	15	3.3
0.10	21	2.5	0.10	20	5.2
0.10	28	4.8	0.10	30	11.1

[a] Average values for at least five runs at each acid concentration. Mean deviation ⩽5%. [b] $[Ru(NH_3)_4(OH_2)^{2+}] = 3.0 \times 10^{-3}$—$7.8 \times 10^{-3}$ mol dm^{-3}; $[Co(NH_3)_4(C_2O_4)^+] = 2.82 \times 10^{-4}$—$7.04 \times 10^{-4}$ mol dm^{-3}. [c] $[Ru(NH_3)_6{}^{2+}] = 2.4 \times 10^{-3}$—$3.6 \times 10^{-3}$ mol dm^{-3}; $[Co(NH_3)_4(C_2O_4)^+] = 1.76 \times 10^{-4}$—$3.52 \times 10^{-4}$ mol dm^{-3}.

given by equation (7) from which we obtain (8). Rearrangement of equation (8) gives (9). A plot of the left-hand side

$$-\,d[Ru^{II}]/dt = k_0[Ru^{II}][Co(NH_3)_5(C_2O_4)^+] + k_1[Ru^{II}][Co(NH_3)_5(HC_2O_4)^{2+}] \quad (7)$$

$$k_{obs.} = (k_0K_a + k_1[H^+])/(K_a + [H^+]) \quad (8)$$

$$k_{obs.}\,(1 + K_a[H^+]^{-1}) = k_0K_a[H^+]^{-1} + k_1 \quad (9)$$

of equation (9) against $[H^+]^{-1}$ should be linear, therefore, with a slope of k_0K_a and an intercept equal to k_1. A least-squares fitting of our data using equation (8) gave an average value of K_a for both ruthenium(II) species reacting with $[Co(NH_3)_5(HC_2O_4)]^{2+}$ of $(9.3 \pm 0.8) \times 10^{-3}$ mol dm^{-3} which is in good agreement with the value of 8.8×10^{-3} mol dm^{-3} obtained by Andrade and Taube [23] for this oxalatocobalt(III) complex. Linear plots of equation (9) using Andrade and Taube's value [23] for K_a were drawn, from which values of k_0 and k_1 were obtained: $[Ru(NH_3)_6]^{2+}$ + $[Co(NH_3)_5(HC_2O_4)]^{2+}$/$[Co(NH_3)_5(C_2O_4)]^+$, $k_0 = 118.1 \pm 10.0$ dm^3 mol^{-1} s^{-1} and $k_1 = 0.50 \pm 0.06$ dm^3 mol^{-1} s^{-1}; $[Ru(NH_3)_5(OH_2)]^{2+}$ + $[Co(NH_3)_5(HC_2O_4)]^{2+}$/$[Co(NH_3)_5(C_2O_4)]^+$, $k_0 = 7.18 \pm 0.74$ dm^3 mol^{-1} s^{-1} and $k_1 = 0.10 \pm 0.02$ dm^3 mol^{-1} s^{-1}.

TABLE 2

Rate constants ($k_{obs.}$) [a] for the oxidation of $[Co(NH_3)_5(HC_2O_4)]^{2+}$ by $[Ru(NH_3)_6]^{2+}$ and $[Ru(NH_3)_5(OH_2)]^{2+}$, $I = 0.20$ mol dm^{-3} (LiCl), 25 °C

$[Ru(NH_3)_5(OH_2)]^{2+}$ + $[Co(NH_3)_5(HC_2O_4)]^{2+}$ [b]		$[Ru(NH_3)_6]^{2+}$ + $[Co(NH_3)_5(HC_2O_4)]^{2+}$ [c]	
$[H^+]$/ mol dm^{-3}	$k_{obs.}$/ dm^3 mol^{-1} s^{-1}	$[H^+]$/ mol dm^{-3}	$k_{obs.}$/ dm^3 mol^{-1} s^{-1}
0.040	1.4	0.040	18.8
0.030	1.7	0.030	27.3
0.025	1.9	0.025	32.6
0.020	2.3	0.020	37.1
0.015	2.8	0.015	44.5
0.010	3.4	0.010	55.3

[a] Average values for at least five runs for each acid concentration. Mean deviation ⩽5%. [b] $[Ru(NH_3)_5(OH_2)^{2+}] = 4.0 \times 10^{-5}$—$5.0 \times 10^{-5}$ mol dm^{-3}; $[Co^{III}] = 5.0 \times 10^{-4}$—$7.5 \times 10^{-4}$ mol dm^{-3}. [c] $[Ru(NH_3)_6{}^{2+}] = [Co^{III}] = 0.8 \times 10^{-4}$—$2.0 \times 10^{-4}$ mol dm^{-3}.

The temperature dependence of $k_{obs.}$ for the oxidation of the two ruthenium(II) species by $[Co(NH_3)_4(C_2O_4)]^+$ was investigated (Table 1), and from the resultant plots of log ($k_{obs.}/T$) against $1/T$ the following activation parameters were obtained.

	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}
$[Ru(NH_3)_6]^{2+}$ + $[Co(NH_3)_4(C_2O_4)]^+$	60.5 ± 5.9	-24.6 ± 3.1
$[Ru(NH_3)_5(OH_2)]^{2+}$ + $[Co(NH_3)_4(C_2O_4)]^+$	66.3 ± 7.1	-11.9 ± 2.8

The temperature dependence of $k_{obs.}$ for the reaction of $[Co(NH_3)_5(HC_2O_4)]^{2+}$ with the two ruthenium(II) species was not investigated due to its composite nature which does not permit sufficiently accurate estimates of k_1.

DISCUSSION

The acid dependence of the oxidation of the two ruthenium(II) species by $[Co(NH_3)_5(HC_2O_4)]^{2+}$ can be explained using equations (4)—(6) with the deprotonated cobalt(III) species reacting very much faster than the starting material, $[Co(NH_3)_5(HC_2O_4)]^{2+}$. The deprotonation (4) and reaction (6) do not apply to $[Co(NH_3)_4(C_2O_4)]^+$, since here oxalate acts as a bidentate ligand, and hence protonation of this ligand would not normally be expected in the acid range used in this study. For this reason, no previous study has reported an acid dependence in any reaction involving $[Co(NH_3)_4(C_2O_4)]^+$.[15,24]

Hexa-ammineruthenium(II) does not possess a readily available substitution site and therefore reduces all the cobalt(III) complexes by an outer-sphere mechanism. The second-order rate constants for the reduction of these oxalatocobalt(III) complexes by $[Ru(NH_3)_5(OH_2)]^{2+}$ are much greater than the usual substitution rates [25] for $[Ru(NH_3)_5(OH_2)]^{2+}$. This reduction should also, therefore, occur by an outer-sphere mechanism. Since outer-sphere reactions are free-energy controlled, the relative reactivities of the two ruthenium(II) species are consistent with their known redox potentials [6,7] {$[Ru(NH_3)_6]^{2+}$: −0.10 V, $[Ru(NH_3)_5(OH_2)]^{2+}$: −0.16 V}.

Coulombic interactions play an important role in these outer-sphere redox reactions. Reduced coulombic repulsion in the outer-sphere precursor complex formed between the unipositive complex $[Co(NH_3)_5(C_2O_4)]^+$ and the ruthenium(II) species, relative to that between the dipositive complex $[Co(NH_3)_5(HC_2O_4)]^{2+}$ and the ruthenium(II) species, partly accounts for why $[Co(NH_3)_5(C_2O_4)]^+$ reacts faster than $[Co(NH_3)_5(HC_2O_4)]^{2+}$. The greater basicity of the deprotonated oxalatocobalt(III) species compared with the protonated species may also account for this reactivity trend.[15] For the same reason, $[Co(NH_3)_5(C_2O_4)]^+$ is reduced by the ruthenium(II) species faster than is $[Co(NH_3)_4(C_2O_4)]^+$.[15]

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