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Kinetics and Mechanism of the Reduction of Penta-amminehalogenocobalt(III) Complexes by Ruthenium(II) Species in Aqueous Solution

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The reactions of the penta-amminehalogenocobalt(III) complexes, $[Co(NH_3)_5X]^{2+}$ (X = F, Cl, Br, or I), with the ruthenium(II) species, $[Ru(en)_3]^{2+}$ (en = ethylenediamine), $[Ru(NH_3)_6]^{2+}$, and $[Ru(NH_3)_5(H_2O)]^{2+}$ have been investigated in aqueous solution at an ionic strength 0.20 mol dm^{-3} [Li(ts); Hts = toluene-*p*-sulphonic acid]. The reactions are acid-independent in the range $[H^+]$ = 0.01—0.20 mol dm^{-3}. Both $[Ru(en)_3]^{2+}$ and $[Ru(NH_3)_6]^{2+}$ react with all the penta-amminehalogenocobalt(III) complexes by an outer-sphere mechanism. The second-order rate constants ($k_F = 3.3 \times 10^{-2}$ dm^3 mol^{-1} s^{-1}, $k_{Cl} = 18.0 \times 10^{-2}$ dm^3 mol^{-1} s^{-1}) for the reduction of the fluoro- and chloro-penta-amminecobalt(III) complexes by $[Ru(NH_3)_5(H_2O)]^{2+}$ lie in the characteristic substitution rate range for $[Ru(NH_3)_5(H_2O)]^{2+}$ and therefore suggest an inner-sphere mechanism for these reactions. Moreover, the reactions involving the fluoro- and chloro-complexes deviate from log-log plots of reactions involving some Co^{III} complexes and ClO_4^-. This is the first instance that $[Ru(NH_3)_5(H_2O)]^{2+}$ is shown to behave as an inner-sphere reductant. The bromo- and iodo-penta-amminecobalt(III) complexes react with $[Ru(NH_3)_5(H_2O)]^{2+}$ by an outer-sphere mechanism, however. Activation parameters measured for the reactions of $[Ru(en)_3]^{2+}$ and $[Ru(NH_3)_6]^{2+}$ with the penta-amminefluorocobalt(III) complex are: $\Delta H^\ddagger$ = (29.4 ± 2.3) kJ mol^{-1}, $\Delta S^\ddagger$ = −(120 ± 15) J K^{-1} mol^{-1} and $\Delta H^\ddagger$ = (47.1 ± 4.2) kJ mol^{-1}, $\Delta S^\ddagger$ = −(50.1 ± 6.0) J K^{-1} mol^{-1} respectively.

The labile and powerful reducing hexa-aqua-ions $[Cr(H_2O)_6]^{2+}$, $[Eu(H_2O)_6]^{2+}$, and $[U(H_2O)_6]^{3+}$ reduce the penta-ammine-halogeno-, carboxylato-, azido-, and thiocyanato-complexes of cobalt(III) [1–4] and ruthenium(III) [5,6] predominantly by an inner-sphere mechanism. The ion $[Ru(NH_3)_5(H_2O)]^{2+}$ is less labile than these hexa-aqua-ions but more labile than $[Ru(NH_3)_6]^{2+}$, as a water molecule occupies its sixth co-ordination sphere. It is therefore a potential inner-sphere reductant also. Recent investigations so far conducted [7–9] in this laboratory as a result of this speculation, however, suggested that $[Ru(NH_3)_5(H_2O)]^{2+}$ is an outer-sphere reductant, even in the presence of good bridging ligands such as carboxylate, azide, or thiocyanate.

A continued investigation of the redox behaviour of $[Ru(NH_3)_5(H_2O)]^{2+}$, herein reported, using in this instance the penta-amminehalogenocobalt(III) complexes as oxidants, was aroused by two observations. First penta-amminefluorocobalt(III) has consistently reacted with the hexa-aqua-ions $[Cr(H_2O)_6]^{2+}$, $[Eu(H_2O)_6]^{2+}$, $[V(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{2+}$, and $[Ti(H_2O)_6]^{3+}$ by an inner-sphere mechanism [1–2,4,10–12] whereas the other penta-amminehalogenocobalt(III) complexes have reacted by either inner- or outer-sphere mechanisms. Thompson and Sykes [12] had interpreted this different behaviour of the fluoro-complex in terms of the ' harder ' nature of the fluoride as a ligand, using the hard acid hard base concept.[13] In the present investigation therefore, it was thought that at least the fluoro-complex will react with $[Ru(NH_3)_5(H_2O)]^{2+}$ by an inner-sphere mechanism. Secondly, $[Ru(NH_3)_5(H_2O)]^{2+}$ reduces the penta-amminehalogenoruthenium(III) complexes [14] by an outer-sphere mechanism. Electronic configuration differences between cobalt(III) and ruthenium(III) exist [5] and often result in mechanistic differences in the redox behaviour of these two metal ions; $[Ru(NH_3)_5(H_2O)]^{2+}$ could therefore reduce the penta-amminehalogenocobalt(III) analogues by an inner-sphere mechanism. Our findings justify our speculations.

Experimental

Materials.—The cobalt(III) complexes $[Co(NH_3)_5X]^{2+}$ (X = F, Cl, Br, or I) were prepared as the chloride salts as described in the literature [15–18] and certified pure by their characteristic u.v.–visible absorption spectra.[16–18] The compound $[Ru(NH_3)_6]Cl_3$ (Johnson Matthey Ltd.), the source of $[Ru(NH_3)_6]^{2+}$, was purified as described previously,[5] $[Ru(NH_3)_5(H_2O)]^{2+}$ was prepared by zinc amalgam reduction of acidic solutions [14] of $[Ru(NH_3)_5I]^{2+}$ in an atmosphere of pure argon gas, and $[Ru(en)_3]^{2+}$ (en = ethylenediamine) was prepared [19] as the tetrachlorozincate salt and fresh acidic solutions of it were made every day and kept over zinc amalgam in an atmosphere of pure argon gas.

Toluene-*p*-sulphonic acid (Hts) (B.D.H.) was recrystallised several times; Li(ts) was prepared and recrystallised several times as described previously.[8]

Kinetics.—The oxidants $[Co(NH_3)_5X]^{2+}$ (X = F, Cl, or Br) have small absorptions in the visible region, with the result that relatively large concentrations of the ruthenium(II) species are required under pseudo-first-order conditions with the ruthenium(II) concentration in large excess (≥10 fold) over cobalt(III). The ruthenium(II) species have relatively limited solubilities and so the reactions of the fluoro-, chloro-, and bromo-complexes were studied at the u.v. absorption peaks of the ruthenium(II) reductants [20] {$[Ru(en)_3]^{2+}$, $\lambda_{max.}$ 302, ε 1 020; $[Ru(NH_3)_6]^{2+}$, $\lambda_{max.}$ 275, ε 670; $[Ru(NH_3)_5(H_2O)]^{2+}$, $\lambda_{max.}$ 300 nm, ε 1 180 dm^3 mol^{-1} cm^{-1}}. At the u.v. absorption peak of the ruthenium(II) species, pseudo-first-order conditions were used for X = F with the three ruthenium(II) species and X = Cl and Br with $[Ru(NH_3)_5(H_2O)]^{2+}$; all with cobalt(III) concentration in large excess (≥10 fold) over ruthenium(II). The reactions of X = Cl and Br with $[Ru(en)_3]^{2+}$ were studied under second-order (equal initial concentrations of both reactants) conditions, and the results of a few runs under pseudo-first-order conditions with the cobalt(III) concentration in excess (≥10 fold) over the ruthenium(II) concentration agree with these within at least 5%. The ion $[Co(NH_3)_5I]^{2+}$ absorbs strongly [12] at $\lambda_{max.}$ 388 nm (ε = 2 700 dm^3 mol^{-1} cm^{-1}), and its reactions with $[Ru(NH_3)_5(H_2O)]^{2+}$ were studied under pseudo-first-order conditions at that wavelength with the ruthenium(II) species in excess (≥10 fold). The slow reactions were studied by conventional devices

Table 1. Specific rate constants ($k_{obs.}$) for the reduction of $[Co(NH_3)_5X]^{2+}$ (X = F, Cl, Br, or I) by Ru^{II} species in aqueous solution, I = 0.20 mol dm^{-3} [Li(ts)], $[H^+]$ = 0.01—0.20 mol dm^{-3}, $[Ru^{II}]_0$ = (0.30—18.70) × 10^{-4} mol dm^{-3} [a]

	$10^4[Co^{III}]_0$ [a]/ mol dm^{-3}	X	θ_c/°C	$k_{obs.}$/ dm^3 mol^{-1} s^{-1}
$[Ru(en)_3]^{2+}$ + $[Co(NH_3)_5X]^{2+}$	19.6	F	25.0	23.0
	30.8	F	25.0	22.9
	49.5	F	25.0	22.5
	20.3	F	32.5	30.5 [b]
	25.2	F	35.5	33.3 [b]
	25.2	F	39.0	37.7 [b]
	0.59	Cl	25.0	130.8
	0.69	Cl	25.0	122.9
	0.81	Cl	25.0	136.5
	0.98	Cl	25.0	132.7
	0.30	Br	25.0	222.1
	0.49	Br	25.0	248.0
	0.59	Br	25.0	233.4
$[Ru(NH_3)_6]^{2+}$ + $[Co(NH_3)_5X]^{2+}$	14.5	F	25.0	81.3
	29.4	F	25.0	80.5
	43.1	F	25.0	80.8
	4.31	F	28.0	113.4 [b]
	29.4	F	32.0	126.6 [b]
	29.4	F	35.5	153.8 [b]
$[Ru(NH_3)_5(H_2O)]^{2+}$ + $[Co(NH_3)_5X]^{2+}$	8.4	F	25.0	3.2×10^{-2}
	12.0	F	25.0	3.1×10^{-2}
	12.8	F	25.0	3.3×10^{-2}
	14.0	F	25.0	3.7×10^{-2}
	50.0	Cl	25.0	18.0×10^{-2}
	60.0	Cl	25.0	20.0×10^{-2}
	72.0	Cl	25.0	17.0×10^{-2}
	4.0	Br	25.0	1.64×10^{2}
	6.0	Br	25.0	1.51×10^{2}
	0.47	I	25.0	2.32×10^{3}
	0.47	I	25.0	2.83×10^{3}
	0.47	I	25.0	2.41×10^{3}
	0.47	I	25.0	2.55×10^{3}

[a] $[Ru^{II}]_0$ and $[Co^{III}]_0$ denote the initial concentrations of the metal ions. [b] Averages of triplicate runs.

on a Pye Unicam SP 500 spectrophotometer and the fast ones on a Durrum-Gibson stopped-flow spectrophotometer. The temperature was kept constant within ±0.1 °C by circulating water from a regulated water-bath around the cell compartment. The ionic strength was maintained at 0.20 mol dm^{-3} with Li(ts), and not $LiClO_4$ because of the instability of the ruthenium(II) species in the latter. Low ionic strength was used as a result of the limited solubility of ruthenium(II) species. A pure argon gas atmosphere was used as a result of the air-sensitivity of the ruthenium(II) species. All reactions conform to linear rate plots to at least four half-lives, and slopes were evaluated using a least-squares program.

Results

The stoicheiometry of each reaction was checked by measuring the ruthenium(II) consumed at its u.v. absorbance peak, under the conditions of a 2—3-fold excess of ruthenium(II) reductant over the cobalt(III) oxidant. In each case, one mole of cobalt(III) consumed one mole of ruthenium(II).

All the kinetic data obtained fit the rate law shown by equation (1), with no systematic trend in the second-order rate

$$-d[Ru^{II}]/dt = k_{obs.}[Ru^{II}][Co^{III}] \qquad (1)$$

constant $k_{obs.}$ for the range of concentrations of the oxidant and reductant at constant temperature (Table 1). The observed second-order rate constants are independent of acid concentration in the range 0.010—0.20 mol dm^{-3} (Table 1). Activation parameters obtained from the temperature variation of the observed second-order rate constants for the reactions of $[Ru(en)_3]^{2+}$ and $[Ru(NH_3)_6]^{2+}$ with $[Co(NH_3)_5F]^{2+}$ are $\Delta H^\ddagger$ = (29.4 ± 2.3) kJ mol^{-1}, $\Delta S^\ddagger$ = −(120 ± 15) J K^{-1} mol^{-1} and $\Delta H^\ddagger$ = (47.1 ± 4.2) kJ mol^{-1}, $\Delta S^\ddagger$ = −(50.1 ± 6.0) J K^{-1} mol^{-1} respectively.

Discussion

The stoicheiometric and kinetic data for the reduction of $[Co(NH_3)_5X]^{2+}$ (X = F, Cl, Br, or I) by $[Ru(NH_3)_6]^{2+}$ and $[Ru(en)_3]^{2+}$ suggest that the reactions can be represented by equations (2) and (3). The ions $[Ru(NH_3)_6]^{2+}$ and $[Ru(en)_3]^{2+}$

$$[Ru(NH_3)_6]^{2+} + [Co(NH_3)_5X]^{2+} + 5H^+ \longrightarrow [Ru(NH_3)_6]^{3+} + Co^{2+} + 5NH_4^+ + X^- \qquad (2)$$

$$[Ru(en)_3]^{2+} + [Co(NH_3)_5X]^{2+} + 5H^+ \longrightarrow [Ru(en)_3]^{3+} + Co^{2+} + 5NH_4^+ + X^- \qquad (3)$$

do not have active substitution sites and therefore react with $[Co(NH_3)_5X]^{2+}$ (X = F, Cl, or Br), by an outer-sphere mechanism [7,15,18] in accordance with equations (2) and (3).

The $[Ru(NH_3)_5(H_2O)]^{2+}$ ion reduces $[Co(NH_3)_5F]^{2+}$ and $[Co(NH_3)_5Cl]^{2+}$ by an inner-sphere mechanism. We suggest two pieces of evidence in support of this conclusion. (*i*) The rate constants for these redox reactions, k_F = 3.3×10^{-2} dm^3 mol^{-1} s^{-1} and k_{Cl} = 18×10^{-2} dm^3 mol^{-1} s^{-1} at 25 °C and I = 0.20 mol dm^3 [Li(ts)] all lie within the range of the charac-

Table 2. Specific rate constants for the reduction of some cobalt(III) complexes and ClO_4^- by $[Ru(NH_3)_6]^{2+}$ and $[Ru(NH_3)_5(H_2O)]^{2+}$ at $I = 0.20$ mol dm^{-3}, $\theta_c = 25$ °C

Oxidant	k_a/dm^3 mol^{-1} s^{-1}	k_b/dm^3 mol^{-1} s^{-1}	Ref.[a]	Ref.[b]
$[Co(NH_3)_5F]^{2+}$	80	3.3×10^{-2}	This work	This work
$[Co(NH_3)_5Cl]^{2+}$	2.6×10^2	18.0×10^{-2}	*c*	This work
$[Co(NH_3)_5Br]^{2+}$	1.6×10^3	1.6×10^2	*c*	This work
$[Co(NH_3)_5I]^{2+}$	6.7×10^3	2.5×10^3	*c*	This work
$[Co(NH_3)_5(SCN)]^{2+}$	3.79×10^2	1.67×10^2	19	7
$[Co(NH_3)_5(NCS)]^{2+}$	0.74	0.28	19	7
$[Co(NH_3)_5(N_3)]^{2+}$	1.82	0.61	19	7
$[Co(NH_3)_5(C_2O_4)]^+$	118.1	7.18	9	9
$[Co(NH_3)_5(HC_2O_4)]^{2+}$	0.50	0.10	9	9
$[Co(NH_3)_4(C_2O_4)]^+$	7.8	3.7	9	9
ClO_4^-	3×10^{-4}	2.6×10^{-2}	23	23

[a] Source of k_a for $[Ru(NH_3)_6]^{2+}$ reactions. [b] Source of k_b for $[Ru(NH_3)_5(H_2O)]^{2+}$ reactions. [c] J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, 1964, **86**, 1686.

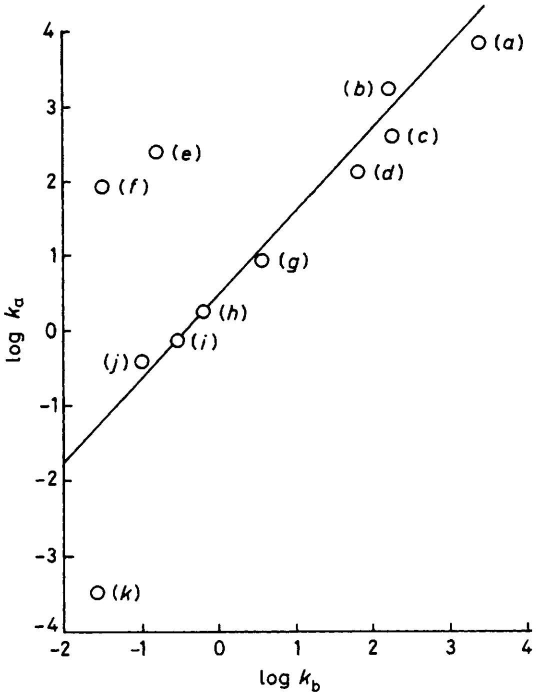

Figure. Log-log plots for the reduction of some cobalt(III) complexes and ClO_4^- by $[Ru(NH_3)_6]^{2+}$ and $[Ru(NH_3)_5(H_2O)]^{2+}$: (*a*) $[Co(NH_3)_5I]^{2+}$, (*b*) $[Co(NH_3)_5Br]^{2+}$, (*c*) $[Co(NH_3)_5(SCN)]^{2+}$, (*d*) $[Co(NH_3)_5(C_2O_4)]^+$, (*e*) $[Co(NH_3)_5Cl]^{2+}$, (*f*) $[Co(NH_3)_5F]^{2+}$, (*g*) $[Co(NH_3)_4(C_2O_4)]^+$, (*h*) $[Co(NH_3)_5(N_3)]^{2+}$, (*i*) $[Co(NH_3)_5(NCS)]^{2+}$, (*j*) $[Co(NH_3)_5(HC_2O_4)]^{2+}$, (*k*) ClO_4^-

teristic substitution [21,22] rate constants for the substitution of various ligands into the co-ordination sphere of $[Ru(NH_3)_5(H_2O)]^{2+}$. Many authors, notably Shepherd and Taube [21] and Persoons and co-workers,[22] had observed that various ligands were substituted into the co-ordination sphere of $[Ru(NH_3)_5(H_2O)]^{2+}$ with $k_{obs.}$ in the range 4.2×10^{-2}—30×10^{-2} dm^3 mol^{-1} s^{-1}. The ClO_4^- oxidises $[Ru(NH_3)_5(H_2O)]^{2+}$ with a second-order rate constant [23] of 2.6×10^{-2} dm^3 mol^{-1} s^{-1} and the mechanism proposed involves substitution of the oxygen atom in ClO_4^- into the co-ordination sphere of $[Ru(NH_3)_5(H_2O)]^{2+}$. We suggest that the reactions of $[Ru(NH_3)_5(H_2O)]^{2+}$ with $[Co(NH_3)_5X]^{2+}$ (X = F or Cl) are therefore substitution-controlled. (*ii*) Log-log plots [7,8,12] for the reduction of various cobalt(III) complexes and ClO_4^- by $[Ru(NH_3)_6]^{2+}$ and $[Ru(NH_3)_5(H_2O)]^{2+}$, based on the data in Table 2, are presented in the Figure. Reactions involving $[Co(NH_3)_5X]^{2+}$ (X = F or Cl) and ClO_4^- fall off the line defined by equation (4) {where k_a

$$\log k_a = (1.05 \pm 0.10) \log k_b \pm 0.40 \qquad (4)$$

represents the rate constants for reactions involving $[Ru(NH_3)_6]^{2+}$ and k_b those involving $[Ru(NH_3)_5(H_2O)]^{2+}$}. The ruthenium(II) species had been previously shown [7,9] to reduce the thiocyanato-, isothiocyanato-, azido-, and oxalato-cobalt(III) complexes by an outer-sphere mechanism, and $[Ru(NH_3)_5(H_2O)]^{2+}$ reduces [23] ClO_4^- by an inner-sphere mechanism. Even though previous investigations [7–9] of the redox behaviour of $[Ru(NH_3)_5(H_2O)]^{2+}$ would suggest an outer-sphere mechanism, this pathway, using $[Co(NH_3)_5X]^{2+}$ (X = F or Cl) as oxidants, was not detected in this study.

The $[Ru(NH_3)_5Cl]^{2+}$ ion was detected and characterised as one of the products of the reactions of $[Ru(NH_3)_5(H_2O)]^{2+}$ with $[Co(NH_3)_5Cl]^{2+}$, by its u.v. absorption peak ($\lambda_{max.}$ 327 nm, ε 1 890 dm^3 mol^{-1} cm^{-1}) after completion of the reaction. This may be looked upon as a third piece of evidence for an inner-sphere mechanism for the reactions of the chloro-complex, but the ruthenium(II) catalysed substitution on ruthenium(III) [6,8] {$[Ru(NH_3)_5(H_2O)]^{3+}$, the oxidised product of $[Ru(NH_3)_5(H_2O)]^{2+}$} makes this conclusion ambiguous.[20]

The $[Co(NH_3)_5X]^{2+}$ (X = Br or I) ions react with $[Ru(NH_3)_5(H_2O)]^{2+}$ by an outer-sphere mechanism, since these fall on the line defined by equation (4) (Figure), and the rate constants for these reactions ($k_{Br} = 1.6 \times 10^2$ dm^3 mol^{-1} s^{-1}, $k_I = 2.5 \times 10^3$ dm^3 mol^{-1} s^{-1}) are several powers of ten greater than the characteristic rate constants for substitution [21,22] on to $[Ru(NH_3)_5(H_2O)]^{2+}$.

Endicott and Taube [23] had reported that $[Co(NH_3)_5I]^{2+}$ and $[Ru(NH_3)_5(H_2O)]^{2+}$ react in part by inner-sphere mechanisms, because $[Ru(NH_3)_5I]^{2+}$ was isolated as a reaction product. Ford [20] has however considered this as ambiguous in view of the possible effects of the ruthenium(II) catalysed substitution on ruthenium(III). Our results for the reactions of $[Co(NH_3)_5X]^{2+}$ (X = Br or I) with $[Ru(NH_3)_5(H_2O)]^{2+}$ have confirmed this ambiguity.

The three ruthenium(II) species $[Ru(en)_3]^{2+}$, $[Ru(NH_3)_6]^{2+}$, and $[Ru(NH_3)_5(H_2O)]^{2+}$ react with $[Co(NH_3)_5X]^{2+}$ (X = F, Cl, Br, or I) in the ' normal ' reactivity [24] order F < Cl < Br < I. Since $[Ru(NH_3)_5(H_2O)]^{2+}$ reacts with $[Co(NH_3)_5X]^{2+}$ (X = F or Cl) by an inner-sphere mechanism, and with $[Co(NH_3)_5X]^{2+}$ (X = Br or I) by an outer-sphere mechanism, the belief that the reactivity sequence among the penta-amminehalogeno-complexes of cobalt(III) and ruthenium(III) is not diagnostic [5,24] of mechanism, but only indicates the relative stabilities of the transition states, is further confirmed by the present study. The $[Ru(NH_3)_5(H_2O)]^{2+}$ ion reduces the penta-amminehalogenoruthenium(III) complexes by an outer-sphere mechanism,[14] but the fluoro- and chloropenta-amminecobalt(III) analogues by an inner-sphere mechanism. Electronic configuration changes accompanying electron transfer processes are $t_{2g}^5 \rightarrow t_{2g}^6$ for ruthenium(III) and $t_{2g}^6 \rightarrow t_{2g}^6 e_g^1$ for cobalt(III).[5] Part of the energetics of these processes may be considerably satisfied by exothermic precursor binuclear complex formation in cobalt(III) complexes, particularly using ' hard ' ligands [13] like F^- and Cl^-. Such energy requirements seem less important for ruthenium(III) complexes and hence they tend to react by an outer-sphere mechanism.

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