Kinetics and Mechanisms of the Electron-transfer Reactions between Uranium(III) and some Ruthenium(III) Ammine Complexes

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The rates of reduction of $[Ru(NH_3)_6]^{3+}$ and $[RuX(NH_3)_5]^{3+}$ (n = 2 or 3; X = H_2O, OH^-, Cl^-, Br^-, and I^-) by U^{3+} have been measured with a stopped-flow spectrophotometer. The reductions of $[Ru(NH_3)_6]^{3+}$ and $[Ru(NH_3)(OH_2)]^{3+}$ proceed by an outer-sphere mechanism. The mechanism for $[Ru(NH_3)_5(OH)]^{2+}$ is less certain, but is probably also outer sphere. The penta-amminehalogeno-complexes have a reactivity order I > Br > Cl, probably by an inner-sphere mechanism. The rates of reduction and reactivity patterns of equivalent cobalt(III) and ruthenium(III) complexes with a common reducing ion are compared. From the results, it is concluded that differences in the kinetic reactivity of the two metal complexes are due to the basic difference in the electronic structure of Co^{III} and Ru^{III}. These differences are manifested as influences of intrinsic factors on the rates and reactivity, and affect not only the rates of the reactions but also the type of mechanism often preferred. On the other hand, a comparison of rates of oxidation of U^{3+} with those of other aqua-ions employing Marcus theory leads to the conclusion that the very low reduction potential of U^{3+} is responsible for its very high redox reactivity.

THERE have been a number of kinetic investigations into the mechanism and reactivity pattern of redox reactions involving complex ions and aqua-ions.[1-4] In many studies, efforts have been directed towards determining the effects of the ligand (bridging [5,6] or non-bridging [7-10]) on the rates and mechanisms of such reactions. A different type of perturbation, which, although of equal importance, has not been given much attention, is the variation of the central metal ion in two analogous metal ammine complexes. Cobalt(III) and ruthenium(III) ammine complexes are good prototypes for this type of study. However, the central metal ions in these two series of complexes differ in one important respect, namely the transferred electron enters the e_g orbitals of Co^{III}, and consequently reduction is accompanied by significant rearrangement of the electronic structure, whereas for Ru^{III} the transferred electron enters a t_{2g} orbital, which is essentially non-bonding, and therefore the central metal ion does not undergo such drastic structural changes on reduction. The influence of this basic difference on the rates and, possibly, the mechanisms of reduction of these complexes is of interest.

Taube and his co-workers [11,12] and Linck and his co-workers [4,13,14] pointed out the importance of such comparisons. However, most of their investigations were conducted with Cr^{2+} and V^{2+} as the reducing aqua-ions. Both these ions exhibit behaviour which reduces their usefulness in drawing broad generalizations applicable to the reactions of other aqua-ions: thus Cr^{2+} reacts with ruthenium(III) complexes by an unusual mechanism in which postcursor complexes are in direct equilibrium with the reactant species,[12] and the reactions of V^{2+} with many cobalt(III) complexes are substitution controlled.[2] Other aqua-ions that have been employed are Yb^{2+} and Sm^{2+} whose reactions with some of these complexes are diffusion controlled,[15] and hence less useful for comparison. It is therefore considered that U^{3+}, which is of intermediate reducing ability between these *d*-block aqua-ions and the lanthanoid ions, and which has not been shown in any of its reactions towards oxidizing ions [16-18] to have any mechanistic peculiarities, will suffice as a good reducing ion for such studies. The kinetics of reduction of some cobalt(III) complexes by U^{3+} have been reported by Espenson and Wang.[16] Our present investigations are of the reduction of some ruthenium(III) ammine complexes by U^{3+}, and the results are compared with those of the equivalent cobalt(III) complexes and with previous results for the bivalent aqua-ions as the reducing agents.

EXPERIMENTAL

Materials.—$[Ru(NH_3)_6]Cl_3$ (Johnson, Mathey) was the source of the ruthenium complexes. It was purified by first dissolving the commercial sample in 10^{-3} mol dm^{-3} HCl, cooling the solution, and adding an equal volume of concentrated HCl to precipitate a purer form of the complex. This process was repeated and the final precipitate was collected by filtration and dried in air. The salts $[RuCl(NH_3)_5]Cl_2$, $[RuBr(NH_3)_5]Br_2$, $[RuI(NH_3)_5]I_2$, $[Ru(NH_3)_5(OH_2)][ClO_4]_3$, and $[Ru(NH_3)_5(OH)]Cl_2$ were prepared by literature methods [19,20] and were identified as pure from the agreement of their spectral characteristics with previously

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reported values. Our values, and those reported by Stritar and Taube [12] and Faraggi and Feder,[15] are presented in Table 1. While there is no difference in the reported absorption peaks from the three independent measurements, our absorption coefficients agree more closely with those of Stritar and Taube, except for $[Ru(NH_3)_5(OH)]Cl_2$ where their value is lower than either that obtained in this work or that reported by Faraggi and Feder. The complex $[Ru(NH_3)_5(OH_2)][ClO_4]_3$ was always used immediately after preparation to avoid contamination with the penta-ammine chloro-complex (maximum at 328 nm). The concentrations of the complexes were generally determined from the absorbances at the maxima and from the determined absorption coefficients. The results were always cross-checked with the concentrations calculated from the amounts of the solid complex dissolved in the solution. All the spectral measurements were made on Unicam SP 800 and SP 500 series II spectrophotometers.

TABLE 1

Spectral data for penta-ammineruthenium(III) ions

	$\lambda_{max.}$/nm			$\varepsilon_{max.}/dm^3\,mol^{-1}\,cm^{-1}$		
Ligand	*a*	*b*	*c*	*a*	*b*	*c*
Cl^-	328	328	327	1 860	1 890	1 810
Br^-	398	398	395	1 845	1 820	1 340
I^-	545	540	545	2 110	2 100	1 960
OH_2	268	268	268	760	730	635
$[OH]^-$	298	295	298	1 901	1 500	1 980

[a] Obtained in this work; reported values of $\varepsilon_{max.}$ are subject to errors not more than 2% of those quoted. [b] From ref. 12. [c] From ref. 15.

Uranium(III) solutions were prepared by zinc-amalgam reduction of uranium(VI) perchlorate which was made by fuming $[UO_2][NO_3]_2\cdot 6H_2O$ with concentrated $HClO_4$ until the Brucine test [21] for nitrogen was negative. Lithium perchlorate was made by neutralization of $Li[CO_3]$ with concentrated $HClO_4$. The resulting solution was boiled to remove CO_2, and the $Li[ClO_4]$ crystals obtained were recrystallized twice from boiled-out distilled water. Sodium chloride, NaBr, and $HClO_4$ were all B.D.H. AnalaR grade, and were used without further purification.

Kinetics.—Rate measurements were made with a Durrum–Gibson stopped-flow spectrophotometer whose flow component is made of Kel-F, and which is also equipped with an accessory that allows the transfer of reactant solutions from capped serum bottles to the spectrophotometer without any contact with air. The course of the reaction was monitored by following the decrease in absorbance of U^{3+} at 350 nm (ε 1 600 $dm^3\,mol^{-1}\,cm^{-1}$).[16,17] Rate measurements were made under pseudo-first-order conditions with concentrations of Ru^{III} at least 10-fold larger than U^{3+}. The ionic strength was maintained constant at $I = 0.25$ mol dm^{-3} with $HClO_4$ and $Li[ClO_4]$, except in the reduction of $[Ru(NH_3)_5(OH)]Cl_2$ where only $Li[ClO_4]$ was used. All the solutions were properly deaerated by bubbling argon that had been passed through towers containing Cr^{2+}.

RESULTS

Pseudo-first-order plots obtained from the smooth absorbance–time traces were all linear to more than 90% completion of reaction for all the complexes studied. From the pseudo-first-order rate constants, second-order rate constants were obtained by dividing each first-order rate constant by the appropriate complex concentration. The derived second-order rate constants were insensitive to changes in the concentrations of the ruthenium(III) complex. This confirms that the reactions are first order in $[U^{3+}]$ and first-order in $[Ru^{III}]$, and hence rate equation (1) describes the kinetic behaviour of these reactions ($X = NH_3$, H_2O,

$$-d\,[Ru^{III}]/dt = -d\,[U^{3+}]/dt = k_0^{X}\,[Ru^{III}][U^{3+}] \quad (1)$$

OH^-, Cl^-, Br^-, or I^-). Values of the individual rate constants (k_0) obtained under different kinetic conditions are given below. Each rate constant represents an average of at least two runs.

$U^{3+} + [Ru(NH_3)_6]^{3+}$.—This reaction adheres strictly to equation (1), and the results are presented in Table 2. At $I = 0.25$ mol dm^{-3} $[H^+] = 0.1$ mol dm^{-3}, and 25 °C, the second-order rate constant $k_0^{NH_3} = (0.95 \pm 0.14) \times 10^5$ $dm^3\,mol^{-1}\,s^{-1}$. The effect of added Cl^- and Br^- on the rate of this reaction was investigated, and the results (Table 2) show that added anions increase the rate of the reaction. Plots of the apparent second-order rate constants ($k_{obs.}$) against $[Cl^-]$ or $[Br^-]$ were linear and fitted equation (2)

$$k_{obs.} = k_0(X) + k_x[X] \quad (2)$$

$X = Cl^-$ or Br^- and $k_0(Cl) = (1.00 \pm 0.15) \times 10^5\,dm^3\,mol^{-1}\,s^{-1}$, $k_{Cl} = (2.8 \pm 0.19) \times 10^6\,dm^6\,mol^{-2}\,s^{-1}$, $k_0(Br) = (0.92 \pm 0.15) \times 10^5\,dm^3\,mol^{-1}\,s^{-1}$, $k_{Br} = (1.52 \pm 0.08) \times 10^6\,dm^6\,mol^{-2}\,s^{-1}$ at $I = 0.25$ mol dm^{-3}, $[H^+] = 0.10$ mol dm^{-3}, and 25 °C. The values of the derived anion-independent rate constants, $k_0(X)$, agree very well with that ($k_0^{NH_3}$) obtained by direct measurement in the absence of any added anion. Activation parameters for the anion-independent path were determined from a least-squares analysis of plots of log $k_0^{NH_3}/T$ against $1/T$. (The $k_0^{NH_3}$ values used were the experimentally determined second-order rate constants when the reaction medium contained neither Cl^- nor Br^-.) The activation parameters were $\Delta H^\ddagger = 3.03 \pm 0.41$ kcal mol^{-1} and $\Delta S^\ddagger = -(25.5 \pm 2.6)$ cal $K^{-1}\,mol^{-1}$.*

TABLE 2

Second-order rate constants, $k_{obs.}$, for the reduction of $[Ru(NH_3)_6]^{3+}$ by U^{3+}. $[U^{3+}] = 1.0 \times 10^{-5}$—$2.0 \times 10^{-5}$, $I = 0.25$ and $[H^+] = 0.1$ mol dm^{-3}

θ_c/°C	$[X^-]$/mol dm^{-3}	$10^4[Ru(NH_3)_6{}^{3+}]$/mol dm^{-3}	$10^{-5}k_0^{NH_3}$ */$dm^3\,mol^{-1}\,s^{-1}$
25.0		1.29	1.05
		1.98	1.00
		2.58	0.83
		3.87	0.92
	0.025 (Cl^-)	4.56	1.70
	0.05	4.56	2.33
	0.10	4.56	4.03
	0.15	4.56	5.50
	0.20	4.56	6.60
	0.025 (Br^-)	4.56	1.25
	0.05	4.56	1.80
	0.10	4.56	2.33
	0.15	4.56	3.00
	0.175	4.56	3.76
	0.20	4.56	4.00
40.0		3.18	1.40
		5.19	1.22
20.0		3.23	0.87
		5.17	0.96
16.0		3.57	0.84
		5.71	0.76

* Average of at least two runs, with values differing by not more than 5%.

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* Throughout this paper: 1 cal = 4.184 J.

[21] F. Feigl, 'Spot Tests in Inorganic Analysis,' Elsevier, Amsterdam, 1958, p. 328.

$U^{3+} + [Ru(NH_3)_5(OH_2)]^{3+}$ *and* $U^{3+} + [Ru(NH_3)_5(OH)]^{2+}$.—The complex $[Ru(NH_3)_5(OH_2)]^{3+}$ reacted with U^{3+} according to equation (1) and the second-order rate constant at $I = 0.25$ mol dm^{-3} $[H^+] = 0.1$ mol dm^{-3}, and 25 °C was $k_0^{\mathrm{OH_2}} = (1.73 \pm 0.12) \times 10^5$ dm^3 mol^{-1} s^{-1}. The effect on the rate of changing the concentrations of the acid and chloride ions was also investigated. The results (Table 3) show that, for the acid range 0.025—0.25 mol dm^{-3}, $k_0^{\mathrm{OH_2}}$ is essentially constant but increases as $[Cl^-]$ increases. Since the value of K_a for reaction (3) is small (pK_a 4.2),[22] the independence of $k_0^{\mathrm{OH_2}}$ of $[H^+]$ implies that either $[Ru(NH_3)_5(OH_2)]^{3+}$ and $[Ru(NH_3)_5(OH)]^{2+}$ react with U^{3+} at the same rate or the

$$[Ru(NH_3)_5(OH_2)]^{3+} \overset{K_a}{\rightleftharpoons} [Ru(NH_3)_5(OH)]^{2+} + H^+ \quad (3)$$

difference in the rate constants for the two complexes is so small that the amount of the hydroxo-complex present in solution is too low to have any observable effect on the rate of reduction of the aqua-complex. The rate of reduction of $[Ru(NH_3)_5(OH)]^{2+}$ was therefore independently measured in a slightly alkaline medium (pH ≈ 7.4), where equilibrium (3) is totally to the left, and the results (Table 3) gave $k_0^{\mathrm{OH}} = 0.95 \times 10^5$ dm^3 mol^{-1} s^{-1} at 25 °C and $I = 0.25$ mol dm^{-3}.

TABLE 3

Second-order rate constants for the reduction of $[Ru(NH_3)_5(OH_2)]^{3+}$ and $[Ru(NH_3)_5(OH)]^{2+}$ by U^{3+} at 25 °C, $I = 0.25$ mol dm^{-3}, and $[U^{3+}] = 1 \times 10^{-5}$—$2 \times 10^{-5}$ mol dm^{-3}

$[H^+]$ / mol dm^{-3}	$10^4[Ru(NH_3)_5(OH_2)]^{3+}$ / mol dm^{-3}	$[Cl^-]$ / mol dm^{-3}	10^{-5} k / dm^3 mol^{-1} s^{-1}
0.1	1.08		1.70
0.1	1.46		1.85
0.1	1.55		1.84
0.1	1.77		1.57
0.1	2.96		1.64
0.025	1.34		1.51
0.038	1.34		1.60
0.10	1.34		1.66
0.25	1.34		1.60
0.10	1.34	0.05	3.81
0.10	1.34	0.10	4.34
0.10	1.34	0.125	6.12
	$10^4[Ru(NH_3)_5(OH)]^{2+}$ / mol dm^{-3}		
pH 7.4 *	1.77		0.98
pH 7.4	2.98		0.93
pH 7.4	3.28		0.95

* Measured at the end of the reaction.

$[RuX(NH_3)_5]^{2+} + U^{3+}$ (X = Cl, Br, *or* I).—The rates of the reactions of these complexes with U^{3+} were first order in $[Ru^{III}]$ and first order in $[U^{3+}]$, and thus conform to rate equation (1). The second-order rate constants obtained were $k_0^{\mathrm{Cl}} = 0.71 \times 10^6$, $k_0^{\mathrm{Br}} = 1.16 \times 10^6$, and $k_0^{\mathrm{I}} \geqslant 2.2 \times 10^6$ dm^3 mol^{-1} s^{-1} at $[H^+] = 0.1$ mol dm^{-3}, $I = 0.25$ mol dm^{-3}, and 25 °C. Values of k_0^{X} at different concentrations of reactants are presented in Table 4. The effect of added Cl^- on k_0^{Cl} was also investigated, but k_0^{Cl} did not vary with changes in $[Cl^-]$. Values of k_0^{Cl} and k_0^{Br} at different temperatures were also determined and from plots of log k_0^{X}/T against $1/T$ the following activation parameters were obtained: $\Delta H_{\mathrm{Cl}}^{\ddagger} = 0.58 \pm 0.46$ kcal mol^{-1}, $\Delta S_{\mathrm{Cl}}^{\ddagger} = -(29.8 \pm 1.0)$ cal K^{-1}mol^{-1}; $\Delta H_{\mathrm{Br}}^{\ddagger} = 0.83 \pm 0.50$ kcal mol^{-1}, $\Delta S_{\mathrm{Br}}^{\ddagger} = -(28.1 \pm 0.6)$ cal K^{-1} mol^{-1}. It should be noted that, although the final product of reduction of the penta-amminehalogeno-complexes is penta-ammineaquaruthenium(II), which can react further as in (4), the rate of reduction of all the ruthenium(III) complexes by U^{3+} is much higher than the rate of reaction (4) and hence interference from this side reaction is insignificant.[12] This conclusion

$$[Ru(NH_3)_5(OH_2)]^{2+} + [RuX(NH_3)_5]^{2+} \xrightarrow{H_2O} 2[Ru(NH_3)_5(OH_2)]^{2+} + X^- \quad (4)$$

is further confirmed by the strict adherence to rate equation (1) for more than 90% completion of the reactions.

DISCUSSION

The assignment of the reactions of ruthenium(III) complexes with such a labile ion as U^{3+} to the inner- or the outer-sphere mechanism can only be unequivocally made for the hexa-ammine complex. The substitution-inertness of this complex, and the non-availability of any ligand with a free electron pair to co-ordinate with the labile U^{3+}, makes this complex a suitable model of an outer-sphere oxidant.[11] The catalytic effect of added chloride and bromide anions, as in other outer-sphere reactions, corroborates this conclusion. The reduction of $[Ru(NH_3)_5(OH_2)]^{3+}$ also most probably occurs by an outer-sphere mechanism. Evidence for this is provided by: (*a*) the catalytic effect of added Cl^- on the rate of reduction of the complex, an effect similar to that on reduction of the hexa-ammine and supposedly character-

TABLE 4

Second-order rate constants for the reduction of $[RuX(NH_3)_5]^{2+}$ (X = Cl, Br, or I) by U^{3+} at $I = 0.25$ mol dm^{-3} and $[U^{3+}] = 2 \times 10^{-6}$—$1 \times 10^{-5}$ mol dm^{-3}

Halide	θ_c / °C	$10^4[Ru^{II}]$ / mol dm^{-3}	$10^{-6}k$ [a] / dm^3 mol^{-1} s^{-1}
Cl^-	25	1.37	0.69
		2.40	0.72
		5.34	0.70
		5.01	0.69
		1.37	0.67 [b]
		1.37	0.70 [c]
	40	2.62	0.86
		4.82	0.74
		1.40	0.86
	20	2.44	0.70
		5.03	0.74
	16	2.54	0.70
		5.28	0.68
Br^-	25	2.48	1.08
		2.99	1.24
	40	1.22	1.28
		1.44	1.30
		1.64	1.31
		2.02	1.32
		2.34	1.28
		1.40	1.06
	20	2.00	0.97
	16	1.40	1.28
		1.62	0.91
		1.80	0.92
		2.40	1.13
I^-	25	0.75	$\geqslant$2.1
		0.95	$\geqslant$2.2

[a] The average of at least two runs. [b] Contains 0.05 mol dm^{-3} Cl^-. [c] Contains 0.1 mol dm^{-3} Cl^-. [d] The rate approached the mixing limit of the equipment, and hence the rate constants are approximate.

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[22] J. A. Broomhead, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, 1964, **3**, 826.

istic of outer-sphere reactions;[16b,23] (*b*) the fact that water is often regarded as at best a very poor bridging ligand.

As for $[Ru(NH_3)_5(OH)]^{2+}$, categorization into the inner- or outer-sphere mechanism from the available evidence is less definitive. In the reactions of aqua- and hydroxo-penta-amminecobalt(III) complexes with aqua-ions, a low value of the ratio $k_0^{OH} : k_0^{OH_2}$ is acceptable evidence of a reaction of the outer-sphere type. However, for ruthenium(III) complexes this criterion is not necessarily valid. As shown in the discussion below, penta-ammineanionocobalt(III) complexes prefer the inner-sphere mechanism because of the large structural changes that accompany reduction, and, consequently, rates of reduction by this mechanism are often much higher than for the outer-sphere mechanism. Since $[OH]^-$ is a very good bridging ligand and the penta-ammineaqua-complex probably reacts by the outer-sphere mechanism, $k^{OH} : k^{OH_2}$ should be large for reactions in which the hydroxo-complex is reduced by an inner-sphere mechanism, and it should be small when the reactions are outer sphere. As for ruthenium(III) ammine complexes, there is no intrinsic preference for the inner-sphere mechanism, and hence there is very little difference in rates of reactions that are of either mechanism. Therefore, a small value of $k^{OH} : k^{OH_2}$, for instance the value of 0.5 : 1 obtained in this work, does not necessarily imply an outer-sphere path for the hydroxo-complex. However, indirect evidence based on the nature of the species present in solution seems to rule out a binuclear transition state with $[OH]^-$ as the bridging ligand in this reaction. At the pH (7.4) in which the reduction of $[Ru(NH_3)_5(OH)]^{2+}$ was studied, both U^{3+} and the product ion U^{4+} should be extensively hydrolysed and exist mostly as $[U(OH)]^{2+}$ and $[U(OH)]^{3+}$ respectively. The higher charge and smaller ionic radius of U^{4+} should presumably make U^{4+} more hydrolysed, and therefore a hydroxide-stabilized binuclear transition state should make the reduction of $[Ru(NH_3)_5(OH)]^{2+}$ more favoured at such a pH; therefore, one would expect $k^{OH} : k^{OH_2} \geqslant 1$ if the reaction occurs by the inner-sphere mechanism. Since this ratio is 0.5 : 1, the reaction probably goes by the outer-sphere mechanism.

The reactions of the penta-amminehalogeno-complexes can be either of the outer- or the inner-sphere mechanism. The only evidence against the former mechanism is the lack of a dependence of k_0^{Cl} on added chloride in the reduction of $[RuCl(NH_3)_5]^{2+}$. The rate pattern for these reactions is $k_0^{I} > k_0^{Br} > k_0^{Cl}$, a reactivity order opposite that obtained for the reduction of the cobalt(III) analogues. Haim[24] pointed out that such a reactivity order is only indicative of the relative stabilities of the transition state, and not diagnostic of mechanism.

For the purposes of comparison, the kinetic parameters obtained in this work and those of Espenson and Wang[16b] for the cobalt(III) analogues are presented in Table 5. The apparent differences in the two systems are: (*a*) rates of reduction of the cobalt(III) complexes have a much wider range (1.3—3×10^6 dm^3 mol^{-1} s^{-1}) than those of Ru^{III} (10^5—10^6 dm^3 mol^{-1} s^{-1}); (*b*) reactions of Ru^{III} that proceed by the outer-sphere mechanism, *viz.* those of $[Ru(NH_3)_6]^{3+}$ and $[Ru(NH_3)_5(OH_2)]^{3+}$, are, at least, a factor of 10^4 faster than their cobalt(III) equivalents, whereas the penta-amminehalogeno-complexes which probably proceed by an inner-sphere mechanism have rates differing by only a factor of 10; (*c*) activation parameters usually measured for only the bromo- and the chloro-complexes show that $\Delta H^‡$ is lower for the ruthenium(III) than for the cobalt(III) reactions. From kinetic data[11-15] on the reduction of these complexes by Cr^{2+}, V^{2+}, Eu^{2+}, and Yb^{2+}, conclusions (*a*)—(*c*) are equally applicable to these systems.

TABLE 5

Kinetic data for the reduction of some ammine complexes of Ru^{III} and Co^{III}

Oxidant [a]	k [b]	$\Delta H^‡$ kcal mol^{-1}	$\Delta S^‡$ cal K^{-1} mol^{-1}	Mechanism [c]
$[Co(NH_3)_6]^{3+}$	1.32			o.s.
$[Ru(NH_3)_6]^{3+}$	9.5×10^4	3.0	−26	o.s.
$[Co(NH_3)_5(OH_2)]^{3+}$	28 [d]			o.s.
$[Ru(NH_3)_5(OH_2)]^{3+}$	1.73×10^5			o.s.
$[Co(NH_3)_5(OH)]^{2+}$	7.6×10^4 [d]			i.s.
$[Ru(NH_3)_5(OH)]^{2+}$	9.5×10^4			o.s.
$[CoCl(NH_3)_5]^{2+}$	3.2×10^4	2.7	−29	i.s.
$[RuCl(NH_3)_5]^{2+}$	7.1×10^5	0.58	−30	i.s.
$[CoBr(NH_3)_5]^{2+}$	1.42×10^4	2.0	−33	i.s.
$[RuBr(NH_3)_5]^{2+}$	1.2×10^6	0.83	−28	i.s.
$[CoI(NH_3)_5]^{2+}$				i.s.
$[RuI(NH_3)_5]^{2+}$	2.2×10^6			i.s.

[a] Data for the cobalt(III) reactions are from ref. 16 while those for Ru^{III} are from this work. [b] $I = 0.2$ (Co^{III}) or 0.25 mol dm^{-3} (Ru^{III}) and 25 °C. [c] o.s. = Outer sphere, i.s. = inner sphere. [d] Estimates from the acid-dependence data given in ref. 16; the estimates were made for the portion for which $k_{obs.} = k_{OH_2} \approx k_1[H^+]^{-1}$ is valid.

The above differences in the kinetic behaviour of ammine complexes of Ru^{III} and Co^{III} towards a common reducing ion can best be rationalized in terms of the two factors that are believed to determine kinetic reactivity in redox systems. These factors, following Marcus[25] and Sutin[26] are (*i*) thermodynamic factors and (*ii*) intrinsic factors. The relative significance of each of these factors in redox reactions has attracted attention.[26,27] However, the data on which the conclusions have been based are mainly from the reactivity patterns of some cobalt(III) complexes in which the ligands are varied. From such comparisons, it has often been concluded that the thermodynamic factors are dominant. The redox potentials[28-30] $E^\ominus$ for the $[Ru(NH_3)_6]^{3+}$–$[Ru(NH_3)_6]^{2+}$, $[Ru(NH_3)_5(OH_2)]^{3+}$–$[Ru(NH_3)_5(OH_2)]^{2+}$,

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$[Co(NH_3)_6]^{3+}$–$[Co(NH_3)_6]^{2+}$, and $[Co(NH_3)_5(OH_2)]^{3+}$–$[Co(NH_3)_5(OH_2)]^{2+}$ couples are 0.10 (or 0.051),[28b] 0.16 (or 0.066),[28b] 0.10, and 0.30 V respectively. Since the affinities of the penta-ammineaqua-complexes of both metal ions for halides differ little, the redox potentials of the penta-amminehalogeno-complexes are likely to be of the same relative magnitudes as those of the aqua-complexes.[12] It is evident from these values and the rate constants in Table 5 that redox potentials, and hence thermodynamic factors, are not responsible for the rate differences in the reduction of ammine complexes of Ru^{III} and Co^{III} by a common reducing ion. Available evidence shows that these complexes $\{[M(NH_3)_6]^{3+}$ and $[M(NH_3)_5(OH_2)]^{3+}\}$ are reduced by the outer-sphere mechanism, and, hence, differences in the stability of the precursor complexes are not relevant when discussing the relative rates of these reactions because no bonds are formed in the transition states. The intrinsic factor must, therefore, be predominant.

TABLE 6

Values of constants employed in the test of Marcus theory for the oxidant $[Ru(NH_3)_6]^{3+}$; $k_{22} = 8.2 \times 10^2$ dm^3 mol^{-1} s^{-1} [a]

Reducing ion	k_{11}	k_{12} [b]	K_{12} [c]	log f	Ref. d	Ref. e
U^{3+}	1.66	9.5×10^4	3.46×10^{12}	−2.06	31	This work
V^{2+}	1.0×10^{-2}	0.80×10^2	1.55×10^6	−0.41	f	11
Yb^{2+}	3.0×10^{-9}	4.5×10^7	1.55×10^{21}	−3.79	15	15
Sm^{2+}	5.0×10^{-12}	2.0×10^8	1.38×10^{28}	−6.12	15	15
Eu^{2+}	1.0×10^{-7}	2.3×10^3	1.41×10^9	−0.74	15 [g]	15

[a] From ref. 28*a*. [b] Values are at ionic strengths of 0.25 for U^{3+}, 0.17 for V^{2+}, and 1.0 mol dm^{-3} for Sm^{2+}, Yb^{2+}, and Eu^{2+}. [c] Calculated from $E^{\ominus}$ values obtained from ref. 29. [d] For k_{11}. [e] For k_{12}. [f] K. V. Krishnamurty and A. C. Wahl, *J. Amer. Chem. Soc.*, 1958, **80**, 5921. [g] D. J. Meier and C. S. Garner, *J. Phys. Chem.*, 1952, **56**, 853.

The basic difference between the two complexes is the electronic configuration of the central metal ion. Electronic-configurational changes accompanying the electron-transfer processes are t_{2g}^5 to t_{2g}^6 for Ru^{III} and t_{2g}^6 to $t_{2g}^6e_g^1$ for Co^{III}. The cobalt reactions are hence accompanied by more drastic internal rearrangements as well as more expensive (in terms of energy requirements) outer-shell solvation changes. Since some of this energy could be obtained from exothermic precursor binuclear complex formation, the cobalt(III) ammine reactions are generally of the inner-sphere type except where this is not structurally possible, in which case the outer-sphere reactions are generally very slow. Such energy requirements are not as high for the ruthenium(III) ammine complexes, and hence the rates of their reactions are not sensitive to either the outer- or inner-sphere mechanism. That the intrinsic factor affects the activation energetics in these reactions and is therefore responsible for the observed differences in rates is also manifested in the higher activation enthalpies obtained for the cobalt(III) reactions (Table 5). From the above, it can therefore be concluded that, while thermodynamic factors might be responsible for the reactivity pattern in reactions where bridging or non-bridging ligands are changed, the influence of intrinsic factors is best investigated by changing the central metal ion in the complexes. The influence of the intrinsic factors is not only limited to differences in rate constants but also extends to the choice of mechanism for the electron-transfer process.

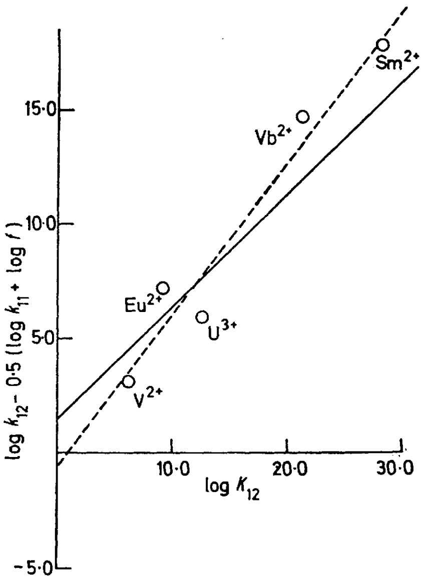
A semiquantitative comparison of the kinetic reactivity of U^{3+} with that of other reducing aqua-ions is best made by application of Marcus theory.[25] For this purpose, equation (5) is employed for cross reactions, where

$$k_{12} = (k_{11}k_{22}K_{12}f)^{\frac{1}{2}} \tag{5}$$

k_{12} is the rate constant for the cross reaction, k_{11} and k_{22} are the homonuclear exchange rates for the reductant and oxidant respectively, and K_{12} is the equilibrium constant for the reaction and is given by (6) where Z is

$$\log f = (\log K_{12})^2/4 \log (k_{11}k_{22}/Z^2) \tag{6}$$

the collision frequency of the uncharged species (usually taken as 10^{11} dm^3 mol^{-1} s^{-1}). Equation (5) applies to reactions that proceed by the same mechanism, and hence we have selected the reduction of $[Ru(NH_3)_6]^{3+}$ by the aqua-ions V^{2+}, Eu^{2+}, Sm^{2+}, Yb^{2+}, Cr^{2+}, and U^{3+}. Values of the parameters employed are presented in Table 6.



Marcus correlation of rate constants with redox potentials for the reduction of $[Ru(NH_3)_6]^{3+}$ by some aqua-ions: (- - - -), least-square plot through the points; (——), theoretical curve with gradient of 0.5 and intercept of 0.5 log k_{22}

Equation (5) can be rewritten in the form (7). Thus,

$$\log k_{12} - 0.5 \log(k_{11} + \log f) = 0.5 \log k_{22} + 0.5 \log K_{12} \quad (7)$$

a plot of the left-hand side of equation (7) against $\log K_{12}$ should be linear with a gradient of 0.5 and an intercept of $0.5 \log k_{22}$. The theoretical curve based on this gradient and intercept, and the actual points based on Table 6, are shown in the Figure. The best linear fit to the curve gives a gradient of 0.67 ± 0.09 and intercept of −0.06 ± 1.64. These values are not far from the expected values of 0.5 and 1.46, particularly when differences in the ionic strength of the media in which k_{12} was obtained and the large errors that may exist in k_{11} (these are mere estimates and not experimentally determined values) for Yb^{2+} and Sm^{2+} are taken into consideration. It can therefore be concluded that equation (5) provides a reasonable semiempirical correlation of the kinetic reactivity of these ions with their redox potentials. Thus the observed reactivity of U^{3+}, relative to the other reductants cited, in the reduction of $[Ru(NH_3)_6]^{3+}$ can be rationalized in terms of the reduction potentials of the reductants. A similar conclusion had earlier[31] been arrived at in the reduction of halogens by U^{3+}.

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