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Studies of the Ruthenium Complexes. XIII. Kinetic Studies of Electron-transfer Reactions between Aquapentaammineruthenium(II) and Halopentaammineruthenium(III) Comlexes

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Kinetic measurements of the electron-transfer reactions from $Ru(OH_2)(NH_3)_5^{2+}$ to $RuX(NH_3)_5^{2+}$, where X=Cl, Br, and I, have been made in aqueous solutions. The reaction rate is independent of the hydrogen-ion concentration, while it is greatly influenced by the ionic strength of the reaction solution. The rate constants were determined to be 147, 172, and 293 $M^{-1} s^{-1}$ for the reaction systems of chloro- bromo- and iodopentaammineruthenium(III) ions respectively at 25 °C in a solution with an ionic strength of 0.0944 M. The activation parameters, ($\Delta H^{\ne}$ kcal mol^{-1}, $\Delta S^{\ne}$ cal K^{-1} mol^{-1}), were (19.4, 16), (18.9, 15), and (11.2, −10) respectively, for the same systems. From the facts that the reaction rate decreases in the order of I>Br>Cl and that the ionic strength of the solution strongly affects the reaction rate, it may be concluded that the present electron-transfer reactions proceed by means of an outersphere-type mechanism.

The reduction reactions of ruthenium(III) ammine complexes have been studied by use of such reductants as Cr(II),[1-3] V(II),[3] the Ru(II) complex,[4] and divalent rare earth ions.[3,5] Since the reduced ruthenium(II) ammines are labile, reactions such as aquation and reoxidation proceed successively to complicate the redox reactions. Electron-transfer reactions from aquapentaammineruthenium(II) to halopentaammineruthenium(III) ions are observed in the radiolysis[6] and the electrochemical reactions.[7,8] However, there have been few quantitative investigations with respect to the kinetics and the reaction mechanism.

The present report will deal with the reaction kinetics of halopentaammineruthenium(III) with the aquapentaammineruthenium(II) ion, and an attempt to elucidate the reaction mechanism will be made on the basis of the kinetic sequences. The reaction rate was spectrophotometrically determined in solutions with various hydrogen-ion concentrations and ionic strengths.

Experimental

Materials. The halopentaammineruthenium(III) halides were prepared from ruthenium trichloride by the previously reported procedures.[9] The complex *p*-toluenesulfonates were recrystallized from a saturated *p*-toluenesulfonate solution. The chemical purities of the products were confirmed spectrophotometrically.[9,10] The reductant, the $Ru(OH_2)(NH_3)_5^{2+}$ ion solution, was prepared from iodopentaammineruthium(III) and zinc amalgam in a deaerated solution with high-purity argon gas. The water was triply distilled.

Procedures. The reductant solution was rapidly added to a deoxygenated solution of the halopentaammineruthenium(III) ion. The pH and the ionic strength of this solution were adjusted with *p*-toluenesulfonic acid and its sodium salt. Before mixing, the solutions were thermostated in a water bath at constant temperatures. The reaction rates were determined by measuring the change in the absorbance at given wave numbers[9] as a function of the reaction time—for instance, at 30.5×10^3 cm^{-1} (ε=1930 M^{-1} cm^{-1}) for chloropentaammine, at 25.1×10^3 cm^{-1} (ε=1980 M^{-1} cm^{-1}) for bromopentaammine, and at 18.5×10^3 cm^{-1} (ε=2050 M^{-1} cm^{-1}) for iodopentaammine. The concentrations of reactants were chosen to be (2—5)$\times 10^{-4}$ M for $RuX(NH_3)_5^{2+}$ and (1—5)$\times 10^{-5}$ M for $Ru(OH_2)(NH_3)_5^{2+}$ in the reaction solution. A Shimadzu UV 200 spectrophotometer was used for all the experiments.

Results and Discussion

The progressive changes in the absorption spectrum are shown in Fig. 1 for the electron-transfer reaction of the chloropentaammine complex. The absorption band at 30.5×10^3 cm^{-1} of the original complexes[9] rapidly decreases as the reaction proceeds. The absorption band at 37.3×10^3 cm^{-1} of the reaction product,[1] $Ru(OH_2)(NH_3)_5^{3+}$, could not be observed since there is an intense absorption of *p*-toluenesulfonate in the region higher than 36×10^3 cm^{-1}. However, this product was identified in a separate experiment[10] in the absence of *p*-toluenesulfonate. Similar changes in the absorption spectrum were observed in the reactions of the other complexes.

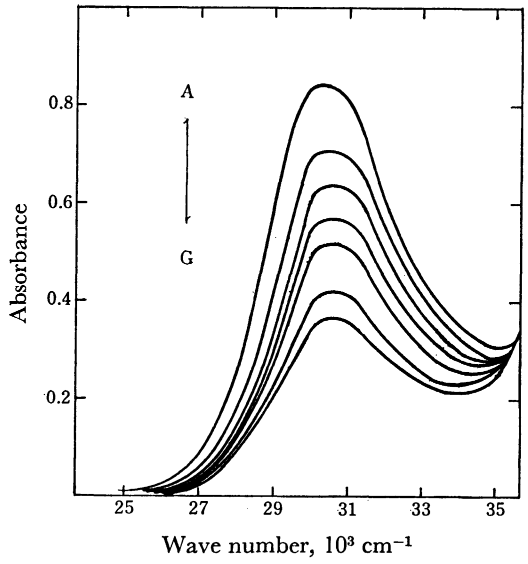

Fig. 1. Changes of absorption spectrum during reduction of $RuCl(NH_3)_5^{2+}$ with $Ru(OH_2)(NH_3)_5^{2+}$ at 30 °C. Curve A is the initial trace followed successively by traces at 25, 50, 85, 125, 180, and 220 (G) sec reaction.

Here, we assumed the following mechanism:

$$\mathrm{Ru^{III}X(NH_3)_5{}^{2+} + Ru^{II}(OH_2)(NH_3)_5{}^{2+}} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{Ru^{II}X(NH_3)_5{}^{+} + Ru^{III}(OH_2)(NH_3)_5{}^{3+}} \quad (1)$$

$$\mathrm{Ru^{II}X(NH_3)_5{}^{+} + H_2O} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{Ru^{II}(OH_2)(NH_3)_5{}^{2+} + X^-} \quad (2)$$

The rate constants have been given[8] as $k_2=6.3\ \mathrm{s^{-1}}$, $k_{-2}=9.0\ \mathrm{M^{-1}\,s^{-1}}$ for the chlorocomplex and $k_2=5.4\ \mathrm{s^{-1}}$, $k_{-2}=5.9\ \mathrm{M^{-1}\,s^{-1}}$ for the bromocomplex at 25 °C and at an ionic strength of 0.1 M. The rate formula with respect to the ruthenium complex in Reactions 1 and 2 can be expressed by Eqs. 3—6:

$$\begin{aligned} &\mathrm{d[Ru^{III}X(NH_3)_5{}^{2+}]}/\mathrm{d}t \\ &= -k_1\mathrm{[Ru^{III}X(NH_3)_5{}^{2+}][Ru^{II}(OH_2)(NH_3)_5{}^{2+}]} \\ &\quad + k_{-1}\mathrm{[Ru^{II}X(NH_3)_5{}^{+}][Ru^{III}(OH_2)(NH_3)_5{}^{3+}]} \quad (3) \end{aligned}$$

$$\begin{aligned} &\mathrm{d[Ru^{II}(OH_2)(NH_3)_5{}^{2+}]}/\mathrm{d}t \\ &= -k_1\mathrm{[Ru^{III}X(NH_3)_5{}^{2+}][Ru^{II}(OH_2)(NH_3)_5{}^{2+}]} \\ &\quad + k_{-1}\mathrm{[Ru^{II}X(NH_3)_5{}^{+}][Ru^{III}(OH_2)(NH_3)_5{}^{3+}]} \\ &\quad + k_2\mathrm{[Ru^{II}X(NH_3)_5{}^{+}]} \\ &\quad - k_{-2}\mathrm{[Ru^{II}(OH_2)(NH_3)_5{}^{2+}][X^-]} \quad (4) \end{aligned}$$

$$\begin{aligned} &\mathrm{d[Ru^{II}X(NH_3)_5{}^{+}]}/\mathrm{d}t \\ &= k_1\mathrm{[Ru^{III}X(NH_3)_5{}^{2+}][Ru^{II}(OH_2)(NH_3)_5{}^{2+}]} \\ &\quad - k_{-1}\mathrm{[Ru^{II}X(NH_3)_5{}^{+}][Ru^{III}(OH_2)(NH_3)_5{}^{3+}]} \\ &\quad - k_2\mathrm{[Ru^{II}X(NH_3)_5{}^{+}]} \\ &\quad + k_{-2}\mathrm{[Ru^{II}(OH_2)(NH_3)_5{}^{2+}][X^-]} \quad (5) \end{aligned}$$

$$\begin{aligned} &\mathrm{d[Ru^{III}(OH_2)(NH_3)_5{}^{3+}]}/\mathrm{d}t \\ &= k_1\mathrm{[Ru^{III}X(NH_3)_5{}^{2+}][Ru^{II}(OH_2)(NH_3)_5{}^{2+}]} \\ &\quad - k_{-1}\mathrm{[Ru^{II}X(NH_3)_5{}^{+}][Ru^{III}(OH_2)(NH_3)_5{}^{3+}]} \quad (6) \end{aligned}$$

In the initial period of the reaction, the concentration of $\mathrm{RuX(NH_3)_5{}^+}$ may be negligibly small, because the rate of aquation (Eq. 2) is large as compared with that of the reverse reaction. In the initial stationary-state period, therefore, Eq. 3 can be simplified to Eq. 7:

$$\begin{aligned} &-\mathrm{d[Ru^{III}X(NH_3)_5{}^{2+}]}/\mathrm{d}t \\ &= k_1\mathrm{[Ru^{III}X(NH_3)_5{}^{2+}][Ru^{II}(OH_2)(NH_3)_5{}^{2+}]} \quad (7) \end{aligned}$$

The plot of $\log\mathrm{[Ru^{III}X(NH_3)_5{}^{2+}]}$ *vs.* the reaction time shows a good linearity for about 60 s after the initiation. The slope of the first-order plot is independent of the initial concentrations of the complex and the hydrogen ion. The rate constants, k_1 calculated from Eq. 7 as a function of the reactant and the hydrogen-ion concentration and of the ionic strength are listed in Table 1. The second-order rate constant, k_1, is independent of the concentrations of the reactants and the hydrogen ion, but increases with an increase in the ionic strength. Applying the simplified Brønsted-Bjerrum-Christiansen formulation,[11] the dependence of the k_1 value on the ionic strength was investigated. Figure 2 shows the relationship between k_1 and the ionic strength, I. The slope of the straight line is nearly +4; this fact suffices to show that the charge product of the reacting particles is four at the transition state of Reaction 1. This effect is similar to those in the reactions of $\mathrm{Ru(NH_3)_6{}^{2+}}$ with $\mathrm{CoX(NH_3)_5{}^{2+}}$, (X=Br, I) and $\mathrm{CoCl_2(en)_2{}^+}$ ions.[2]

TABLE 1. THE RATE CONSTANTS OF THE ELECTRON-TRANSFER REACTIONS OF $\mathrm{RuCl(NH_3)_5{}^{2+}}$ WITH $\mathrm{Ru(OH_2)(NH_3)_5{}^{2+}}$ AT (30±1) °C

$\mathrm{[Ru^{III}Cl(NH_3)_5{}^{+}]}$ 10^{-4} M	$\mathrm{[Ru^{II}(OH_2)(NH_3)_5{}^{2+}]}$ 10^{-5} M	I 10^{-2} M	$\mathrm{[H^+]}$ 10^{-2} M	k_1 $\mathrm{M^{-1}\,s^{-1}}$
3.36	4.77	9.44	9.44	158
3.98	4.77	9.44	9.44	173
5.06	4.77	9.44	9.44	161
4.69	1.14	9.44	9.44	173
4.37	1.97	9.44	9.44	159
4.07	2.79	9.44	9.44	165
2.77	2.99	9.44	9.44	172
3.06	4.44	9.44	3.15	163
5.61	4.44	9.44	6.35	167
				Av 166±6
2.96	3.89	12.10	9.44	179
2.96	3.87	14.00	9.44	199
3.21	3.89	16.10	9.44	216
3.73	3.89	18.80	9.44	250
3.51	3.89	29.10	9.44	265

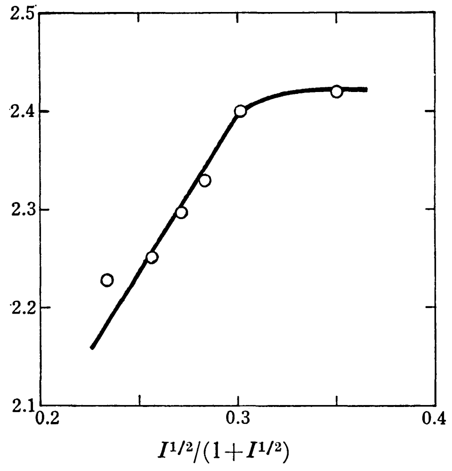

Fig. 2. Effect of ionic strength on the electron transfer reaction rate of RuCl $\mathrm{(NH_3)_5{}^{2+}}$ with $\mathrm{Ru(OH_2)}$ $\mathrm{(NH_3)_5{}^{2+}}$ at 30 °C, $\mathrm{[H^+]}=0.0944$ M.

The curve-fitting method with various k_{-1} values was applied to the reaction between $\mathrm{RuCl(NH_3)_5{}^{2+}}$ and $\mathrm{Ru(OH_2)(NH_3)_5{}^{2+}}$ using the values of $k_1=147\ \mathrm{M^{-1}\,s^{-1}}$, $k_2=6.3\ \mathrm{s^{-1}}$, and $k_{-2}=9.0\ \mathrm{M^{-1}\,s^{-1}}$. As is shown in Fig. 3, the experimental plot of the concentration variation for the $\mathrm{RuCl(NH_3)_5{}^{2+}}$ species falls on the calculated curve when $k_{-1}\leq 100\ \mathrm{M^{-1}\,s^{-1}}$. The concentration variations of the other species in Reactions 1 and 2 were calculated by means of the numerical integration of Eqs. 3—6 using the same values of the rate constants. The results are also given in Fig. 3. The concentration of the intermediate, $\mathrm{[RuCl(NH_3)_5{}^+]}$, is less than those of the other species by a factor of about 10^{-2}—10^{-3}, and it instantly reaches a maximum after the initiation of the reaction. The concentration of $\mathrm{[Ru(OH_2)(NH_3)_5]^{2+}}$ decreases momentarily upon initiation, and then it increases very slowly.

The kinetic parameters for the electron-transfer reactions of the halogenopentaamminerutheium(III) complexes are exhibited in Table 2, along with those for the reference reactions. All the rate constants are determined in the solution with I=0.094 M. The order of the magnitude of the rate constants is chloropentaammine< bromopentaammine<iodopentaammine. This order is not the same as that of 3.5×10^4 M^{-1} s^{-1}>2.2×10^3 M^{-1} s^{-1}>2.6×10^2 M^{-1} s^{-1} estimated on the basis of the analysis of catalytic reactions involved in the process of the electron transfer between halogenopentaammines and Cr(II).[3] The relative rates (chloro: bromo: iodo) are 135: 8: 1 for the Cr(II) reaction and 57: 12: 1 for the reaction with Eu(II). On the other hand, the relative rates are 1: 1.7:—[12] for the V(II) reaction, and 1: 1.2: 2.0 at 25 °C or 1: 1.7: 2.4 at 30 °C for the present reaction with $Ru(OH_2)(NH_3)_5^{2+}$. The reactions of the ruthenium(III) halopentaammines with Cr(II) and Eu(II) are inner-sphere, while the reactions with V(II) are of the outer-sphere type.[3] This similarity in the relative reactivity may support the theory that the present reaction has an outersphere mechanism.

An outersphere process often occures when both reactants of the electron-transfer reaction are inert to substitution over the period required for the electron-transfer process. A typical reaction can be found in a homonuclear self-exchange electron transfer such as the reaction between $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_6^{2+}$ ions.[4] In the present study, all of the oxidants contain halide ligands which can interact with the reducing cation,

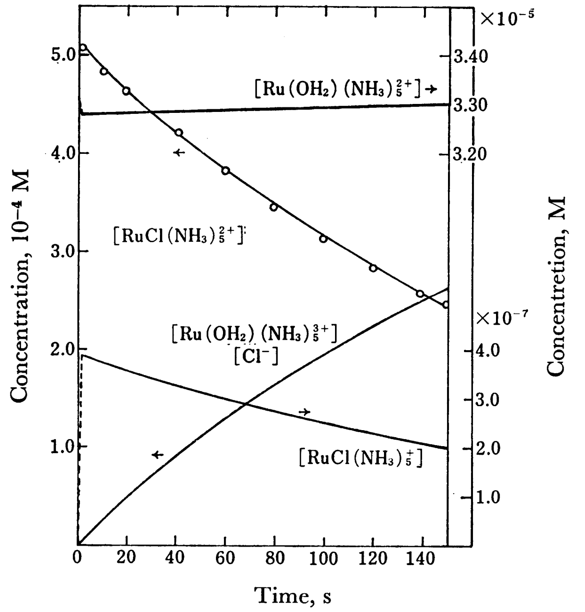

Fig. 3. Concentration variation of chemical species participating in the electron transfer reaction of $RuCl(NH_3)_5^{2+}$ with $Ru(OH_2)(NH_3)_5^{2+}$ at 25 °C, $[RuCl(NH_3)_5^{2+}]_{t=0}=5.10\times10^{-4}$ M, $[RuOH_2(NH_3)_5^{2+}]_{t=0}=3.32\times10^{-5}$ M, $I=[H^+]=0.0944$ M.
○: Experimental, —: calculated.

Table 2. Kinetic parameters for the electron-transfer reactions of halogenopentaammineruthenium(III) complexes

Reaction system	k_1 M^{-1} s^{-1} (temp °C)	$\Delta H^{\ddagger}$ kcal mol^{-1}	$\Delta S^{\ddagger}$ cal K^{-1} mol^{-1}
$RuCl(NH_3)_5^{2+}$-$Ru(OH_2)(NH_3)_5^{2+}$ [a]	32±2 (16) 147±5 (25) 166±6 (30)	19.4	16
-Cr^{2+} [b]	3.5×10^4(25)	1.3	−33
-V^{2+} [b]	3.0×10^3(25)	3.8	−30
-Eu^{2+} [b,c]	1.5×10^4(25), 2.4×10^4(25)	—	—
-Sm^{2+} [c]	1.5×10^8(25)	—	—
-Yb^{2+} [c]	1.5×10^7(25)	—	—
-e_{aq} [c]	6.0×10^{10}(25)	—	—
$RuBr(NH_3)_5^{2+}$-$Ru(OH_2)(NH_3)_5^{2+}$ [a]	52±2 (15) 106±4 (20) 172±8 (25) 286±8 (30)	18.9	15
-Cr^{2+} [b]	2.2×10^3(25)	2.8	−34
-V^{2+} [b]	5.1×10^3(25)	2.8	−34
-Eu^{2+} [b,c]	$\approx3\times10^3$(25), 1.3×10^9(25)	1	−37
-Sm^{2+} [c]	1.5×10^8(25)	—	—
-Yb^{2+} [c]	3.3×10^7(25)	—	—
-e_{aq} [c]	5.0×10^{10}(25)	—	—
$RuI(NH_3)_5^{2+}$-$Ru(OH_2)(NH_3)_5^{2+}$ [a]	140±5 (15) 225±8 (20) 293±7 (25) 396±9 (30)	11.2	−10
-Cr^{2+} [b]	2.6×10^2(25)	—	—
-Eu^{2+} [c]	2.6×10^2(25)	—	—
-Sm^{2+} [c]	$\approx10^8$(25)	—	—
-Yb^{2+} [c]	$\approx10^8$(25)	—	—
-e_{aq} [c]	$\approx6\times10^{10}$(25)	—	—
$Ru(NH_3)_6^{3+}$-$Ru(NH_3)_6^{2+}$ [d]	437±51 (15) 843±69 (25)	10.3±1.0	−11±3

a) Present work, $I=[H^+]=0.094$ M. b) Ref. 3. c) Ref. 5. d) Ref. 4.

while the reductant has a water molecule in the coordination sphere which is weakly capable of reacting with the oxidizing cation. The rate constants for the aquation of halogenopentaammineruthenium(III) have been determined to be 3.28×10^{-4} s^{-1} for the chlorocomplex, 3.99×10^{-4} s^{-1} for the bromocomplex, and 1.64×10^{-4} s^{-1} for the iodocomplex at 54.5 °C.[13] These values are smaller than those of the pseudo-first-order rate constants for the correspondings electron-transfer reactions. The rate constants for the anations of the chloride and bromide ions to $Ru(OH_2)(NH_3)_5^{2+}$ have been determined to be 9.0 $M^{-1}\,s^{-1}$ and 5.9 $M^{-1}\,s^{-1}$ at 25 °C respectively.[8] These values are also smaller than those for the electron-transfer reactions. Thus, the substitution on either $RuX(NH_3)_5^{2+}$ or $Ru(OH_2)(NH_3)_5^{2+}$ is not rate-determing; hence, the outersphere mechanism is applicable to the present electron-transfer reactions.

In Table 2, the values of both $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are practically the same for the reactions of chloro and bromopentaammines, and for the reactions of the $RuI(NH_3)_5^{2+}$-$Ru(OH_2)(NH_3)_5^{2+}$ and $Ru(NH_3)_6^{3+}$-$Ru(NH_3)_6^{2+}$ systems. This suggests that the energy change to form the reaction intermediate is the same for both the reaction systems. The electron-transfer reactions of halopentaammines with the simple metal ions are characterized by small values of $\Delta H^{\neq}$ and large negative values of $\Delta S^{\neq}$. The reactions with Cr_{aq}^{2+} and Eu_{aq}^{2+} are regarded as of the innersphere type,[3,5] while the reaction with V_{aq}^{2+} is accounted for by the outersphere mechanism.[3] Hence, it is inadequate to distinguish the innersphere and outersphere mechanisms by only the aid of the activation parameters.

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