Studies of Ruthenium Complexes. IV. The Solvent Effect on the Isotopic Ligand-exchange Reaction of the *cis*-Dibromotetraammineruthenium(III) Complex

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The isotopic ligand-exchange reactions of *cis*-dibromotetraammineruthenium(III) were studied in aqueous and methanol–water solutions in order to distinguish them from those in the case of the monobromocomplex and in order to ascertain the role of the water molecule with respect to the reaction mechanism. In an aqueous solution, the reaction proceeds through the rate-determining aquation step with the S_N2 mechanism: $Ru(NH_3)_4Br_2^+ + H_2O \rightarrow Ru(NH_3)_4(H_2O)Br^{2+} + Br^-$, $Ru(NH_3)_4(H_2O)Br^{2+} + {}^*Br^- \rightarrow Ru(NH_3)_4Br{}^*Br^+ + H_2O$. This result is similar to that for the monobromocomplex. In the methanol solution ($H_2O \sim 1.5\%$), the exchange reaction proceeds through the S_N1 mechanism: $Ru(NH_3)_4Br_2^+ \rightarrow Ru(NH_3)_4Br^{2+} + Br^-$, $Ru(NH_3)_4Br^{2+} + {}^*Br^- \rightarrow Ru(NH_3)_4Br{}^*Br^+$. When the concentration of water becomes very low, the number of solvated water molecules decreases; therefore, the coordinated bromide ion may easily be liberated. When the concentration of water is higher than 10%, the rate constant increases with the increase in the water concentration. Since the electronic spectra did not change during the exchange reaction, it would seem that the water molecule attacks a *cis*-position as a nucleophile. These results can be interpreted by postulating a hydrogen-bond between the proton of the water molecule and the coordinated bromide ion.

In our previous work,[1] it was found that the rate-determining step in the isotopic ligand-exchange reaction of halogenopentaammineruthenium(III) is the aquation process, which proceeds through the S_N2 mechanism, however, the role of the water molecule in connection with this reaction was not yet clear. For this purpose, it was necessary to use a considerably soluble complex in a mixed solution of methanol and water, because the monohalogenopentaamminecomplexes are less soluble in this solution. Thus, the *cis*-dibromotetraammine complex was chosen as a basis for a study of the ligand-exchange reaction.

In the present paper, the comparison of the reaction rate in the cases of mono- and dibromocomplexes in aqueous solutions, and the reaction mechanisms for the latter complex in a methanol–water solution, will be discussed in connection with those in the aqueous solution.

Experimental

Reagents. All the chemicals used were of a reagent grade. The radio-isotope, $^{82}Br(NH_4Br)$, was obtained from the Japan Radioisotope Association, Tokyo, and was used as a radioactive tracer. Doubly-distilled water was used in all the kinetic runs. The ionic strength and the acidity of the reaction mixture were adjusted with *p*-toluenesulfonic acid and its sodium salt. The sodium salt was prepared by the neutralization of the acid with sodium hydroxide.

Preparation of Complexes and Kinetic Measurements. Chloropentaammineruthenium(III) was dissolved in an ammonia solution, and then transformed into a hydroxo-complex. Oxalic acid was subsequently added to make the solution acidic. This solution was heated for about ten minutes, after it has then been cooled, sodium dithionate was added and the solution was left alone. The yellow precipitates thus obtained consisted of *cis*-$[Ru(NH_3)_4C_2O_4]_2S_2O_6$, and the molar extinction coefficient was $4.87 \times 10^3\ M^{-1}\ cm^{-1}$ (at 283 mμ).

Concentrated hydrobromic acid was added to this oxalatocomplex, and the solution was heated for a few minutes. When the electronic spectrum showed *cis*-$Ru(NH_3)_4Br_2^+$, ethanol was added to isolate *cis*-$[Ru(NH_3)_4Br_2]Br$ as a precipitate. The final product was obtained by three recrystallizations from distilled water. The molar extinction coefficient of this compound was $1.67 \times 10^3\ M^{-1}\ cm^{-1}$ (at 442 mμ) and $1.22 \times 10^3\ M^{-1}\ cm^{-1}$ (at 370 mμ).

Found: H, 2.91; N, 13.82%. Calcd for $[Ru(NH_3)_4Br_2]Br$: H, 2.94; N, 13.70%.

The procedures of kinetic measurement and the apparatus and technique for radiometry used in this work were similar to those already described.[1] A reaction vessel with a refluxing apparatus was used to avoid the loss of any volatile material. A Hitachi Model 124 spectrophotometer was used to determine the absorption spectra of the complexes.

Results and Discussion

Estimation of the Exchange Rate, R, and the Rate Constant, k_{ex}. The reactions have been carried out for a period of 8—10 times half-time, and the exchange rates were calculated by means of McKay's equations.[2]

$$\ln(1 - X/X_\infty) = -[(a+b)/ab]Rt \qquad (1)$$

$$R = 0.693ab/[(a+b) \cdot T_{1/2}] \qquad (2)$$

where R is exchange rate; t, time; a and b, the initial concentrations of the complex and the halide ion, and X and X_∞, the radioactivity of the *cis*-dibromotetraammine complex at time t and at an infinite time. From the plots in Fig. 1, the half-time of the exchange reaction was determined.

From the measurements of the reaction rates varying

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[1] T. Shinohara T. Yamada N. Takebayashi, S. Hiraki, and A. Ohyoshi, This Bulletin, **45**, 3081 (1972).

[2] H. A. C. McKay, *J. Amer. Chem. Soc.*, **65**, 702 (1943).

TABLE 1. RATE CONSTANTS (AT 70 °C) AND ACTIVATION PARAMETERS FOR LIGAND-EXCHANGE REACTIONS

Complex ion	k_{ex}(sec^{-1})	E_a(kcal/mol)	ΔS(e.u.)
$Ru(NH_3)_5Br^{2+}$	1.5×10^{-4}[a]	23.2 ± 0.9	-9 ± 2
cis-$Ru(NH_3)_4Br_2^+$ in aqueous solution	4.8×10^{-4}	$23\ \pm3$	-7 ± 8
in 98.5% Metanol solution	4.2×10^{-4}[b]	24.8 ± 0.6	-0.1 ± 0.1

a) This value was obtained by extrapolating the value obtained at 80 °C.
b) This value was obtained by extrapolating the value obtained at 55 °C.

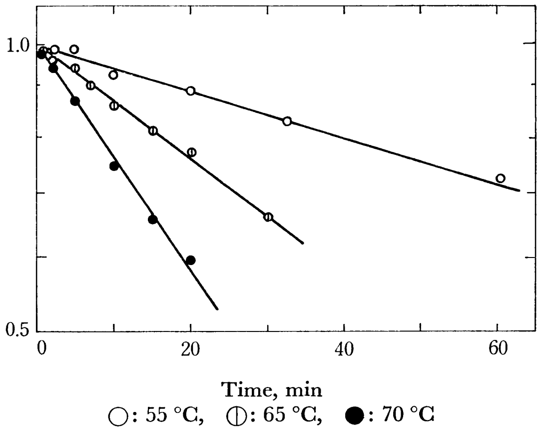


Fig. 1. Plots of log(1 − X/X_∞) *vs.* reaction time.

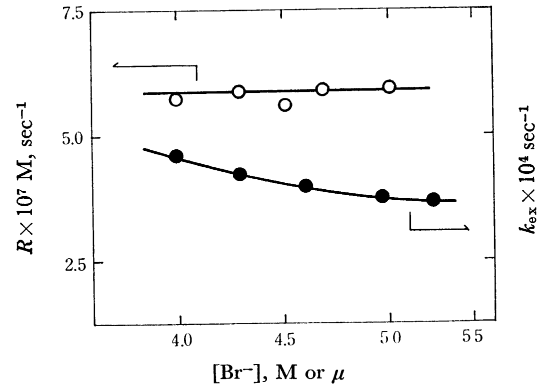
with the concentration of the complex in aqueous and methanolic solutions, it is found that both the exchange reactions are first-order with respect to the concentration of the complex. No influence of the concentrations of the bromide ion and the hydrogen ion on the reaction rate has been observed, and no practical salt effect on the rate is found in either solution. Thus, the reaction rate, R, and the rate constant, k_{ex}, can be expressed by the following equations, just as in the case of the monobromopentaammine complex.[1]

$$R = k_{ex}[\text{complex}] \qquad (3)$$

$$k_{ex} = 0.693b/[(a+b)\cdot T_{1/2}] \qquad (4)$$

The values of the rate constants of the exchange reactions are listed, along with that of the reference reaction, in Table 1.

Ligand-exchange Reaction of the cis-*Dibromotetraammine Complex in an Aqueous Solution.* To ascertain the dependence of the rate on the ionic strength, experiments were carried out while varying the ionic strength of the aqueous solution from 4.0 to 5.0 using sodium *p*-toluenesulfonate. From the plot of k_{ex} *vs.* ionic strength (Fig. 2), it was found that the rate constant decreases slightly with the increase in the ionic strength. By succesive measurements of the absorption spectrum of the reaction solution, it was confirmed that the exchange reaction was accompanied by aquation as a side reaction. The extent of this decomposition was about 9% when 8 times the half-time had elapsed at the ionic strength of 5.0.



Conditions for measurement of R
[complex]: 0.015 M, [H$^+$]: 4.0M, μ=5.0

Fig. 2. Effects of bromide-ion concentration and ionic strength on the exchange rate in aqueous solution at 70 °C.

It is plausible that the exchange rate is essentially independent of the ionic strength; therefore, the charged species is not involved in the rate-determining step. Thus, it may be concluded that the exchange reaction proceeds through the aquation process (5) and that the anation reaction (6) follows:

$$cis\text{-}Ru(NH_3)_4Br_2^+ + H_2O \longrightarrow cis\text{-}Ru(NH_3)_4BrOH_2^{2+} + Br^- \qquad (5)$$

$$cis\text{-}Ru(NH_3)_4BrOH_2^{2+} + {}^*Br^- \longrightarrow cis\text{-}Ru(NH_3)_4Br{}^*Br^+ + H_2O \qquad (6)$$

The former step is presumably the rate-determining one. These reaction schemes are similar to those of the monobromocomplex.[1]

The rate constant of the dibromocomplex is nearly three times greater than that of the monobromocomplex (Table 1). The difference between these rate constants may be statistically understood, as will be described below.

In the aquation reaction of halogenoamminecobalt(III), the rate constant for the *cis*-dichlorotetraammine complex is 100 times that for monochloropentaammine.[3] On the basis of this evidence, it was concluded that the aquation reaction proceeded by means of the S_N1 mechanism.

In the present study, such a discrepancy between the two rate constants is seen to be small in comparison with that in the above case. It would seem that the dissociative mechanism could not be involved in the rate-determining step expressed by Eq. (5). From the measurements of the absorption spectra in the present study, it was found that the steric configuration of the *cis*-dibromocomplex was retained during the exchange reaction. This fact suggests that the water molecule enters from the front side of coordinated bromide ions. The process of Eq. (5) involves an intermediate which is formed by hydrogen bondings between coordinated bromide-ions and the protons of the water molecule, that is, the S_N2 Front-side mech-

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3) R. G. Pearson, C. R. Boston, and F. Basolo, *J. Phys. Chem.*, **59**, 304 (1955).

anism. This mechanism has also been reported in the acid-hydrolysis reaction of *cis*-dihalogenodiethylendiammineruthenium(III) by Broomhead and Maguire.[4)]

The fact that the exchange rate for the dibromocomplex is three times as fast as that for the monobromocomplex can be interpreted by indicating that the probability of the hydrogen-bond formation in the former case is twice as much as that in the latter case.

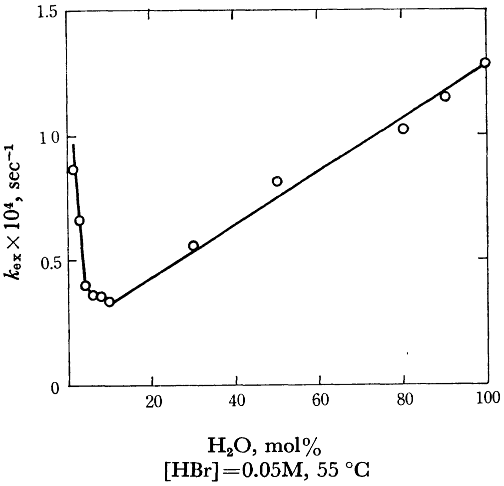


Fig. 3. Effect of water concentration on the exchange rate constant.

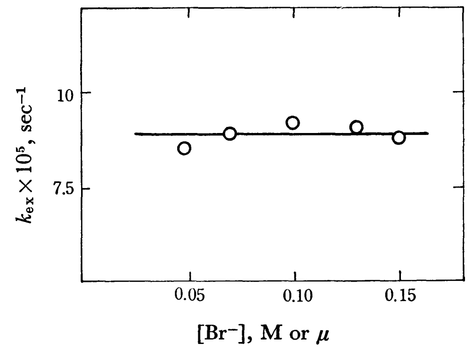
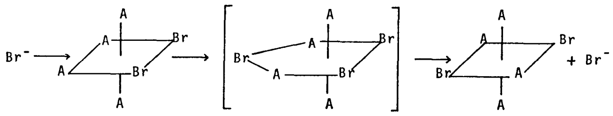


Fig. 4. Effects of bromide-ion concentration and relative ionic strength on the rate constant in 98.5% methanol solutions at 55 °C.

Exchange Reaction in Water-Methanol Mixed Solutions. In the aqueous solution, the ligand exchange reaction was found to proceed through the S_N2, F.S. mechanism. To ascertain the role of water molecule for the reaction mechanism, therefore, experiments were carried out varying the water concentration with a methanol solvent. The plot of the observed rate constant *vs.* the water content (mol %) in a methanol solution is shown in Fig. 3. In the region where the concentration of water is lower than 10%, the sign of the slope is negative, while it is positive in the concentration region higher than 10%. It appears that the water molecule behaves as a nucleophile in the rate-determining process (5). This action of the water molecule gives an evidence for the S_N2, F.S. mechanism discussed in a previous paragraph. When the water concentration is less than 10%, the exchange reaction mechanism may be different from the above one; that is, the following mechanisms may be presumed: (1) the S_N1 dissociative mechanism, (2) a S_N2 mechanism involving the bromide-ion as a nucleophile, or (3) a mechanism which involves methoxide ion or methanol molecule in the intermediate. The last mechanism is the most improbable, because it is difficult for the methoxide to exist in a hydrogen-ion solution of 0.05 M and a methanol molecule has even less coordination ability. To distinguish the S_N1 mechanism (1) from the S_N2 mechanism (2), both the concentration of the bromide ion and the ionic strength were varied. As is shown in Fig. 4, on neither the bromideion concentration nor the ionic strength depends the exchange rate constant; that is, both the bromide ion and charged species are not involved in the rate-determining step, and the S_N2 mechanism may be concluded to be impossible. Moreover, when the S_N2 mechanism proceeds, the bromide-ion should attack the bromide ligands from the opposite side because a front-side attack is difficult because of the electrostatic repulsion between the nucleophile-bromide and the ligand-bromide ions. This is schematically expressed by Eq. (7):



(7

For this reason, the reaction product should be a *trans*-isomer. Since there is no change in the absorption spectrum during the exchange reaction, no isomerization of the *cis*-dibromocomplex occurs; therefore, the S_N2 mechanism (2) is also improbable. As for the remaining mechanism, that is, the dissociative

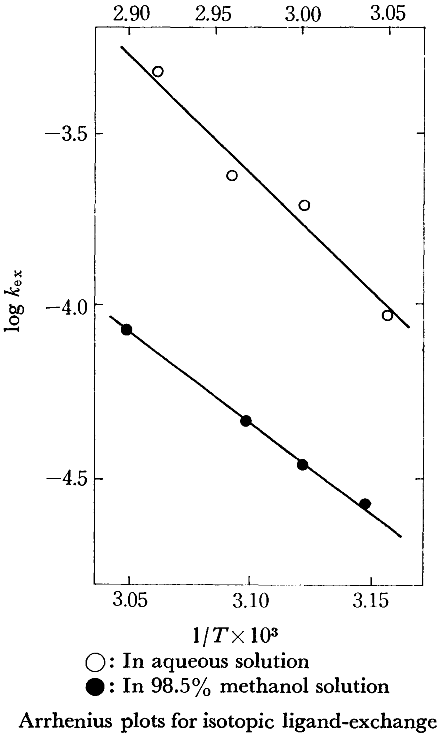


Fig. 5. Arrhenius plots for isotopic ligand-exchange reactions.

[4)] J. A. Broomhead and L. Kane-Maguire, *Inorg. Chem.*, **7**, 2519 (1968).

S_N1 mechanism may be considered acceptable on the basis of the following explanation. The rate constant increases with the decrease in the water concentration in the region less than 10% (Fig. 3). When the water concentration is comparatively high, the solvated water molecule in the second coordination sphere can be repressed until the bromide ion dissociates. When the water concentration is extremely low, the decrease in the solvated molecule facilitates the dissociation of the bromide ion. Thus, it may be concluded that the exchange reaction proceeds through two reaction processes, (8) and (9), and that the former using the S_N1 mechanism is the rate-determining step.

$$\textit{cis}\text{-Ru(NH}_3)_4\text{Br}_2{}^+ \longrightarrow \text{Ru(NH}_3)_4\text{Br}^{2+} + \text{Br}^- \quad (8)$$

$$\text{Ru(NH}_3)_4\text{Br}^{2+} + {}^*\text{Br}^- \longrightarrow \textit{cis}\text{-Ru(NH}_3)_4\text{Br}^*\text{Br}^+ \quad (9)$$

Figure 5 shows the Arrhenius plots, while the activation parameters are listed, along with those of the reference reactions, in Table 1. The values of the activation energies are nearly the same for all the reactions, though the value of the activation entropy for the reaction in the 98.5% methanol solution is extremely small. The degree of entropy change in the transition state of the S_N1 mechanism was estimated to be $-2\sim-20$ e.u. for the aquations of carboxylatopenta-ammineruthenium(III) in aqueous solutions.[5] The small value of entropy change for the same mechanism in the methanolic solution may be ascribed to the poor solvation ability of the methanol molecule compared with that of the water molecule.

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5) A. Ohyoshi, A. Jyo, and N. Shin, This Bulletin, **45**, 2121 (1972).