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Studies of Ruthenium Complexes. III. Kinetics of Isotopic Ligand-Exchange Reactions of Halogenopentaammineruthenium(III) Complexes in Aqueous Solution

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Kinetic studies of isotopic ligand-exchange reactions, $[Ru(NH_3)_5X]^{2+}+X^{*-}=[Ru(NH_3)_5X^*]^{2+}+X^-$, where X=Cl, Br, and I, have been made in aqueous solutions. The effects of the hydrogen- and halide-ion concentrations, and of the ionic strength of the aqueous solution on the exchange rate had not been observed under certain definite experimental conditions. The rate constants were determined to be $3.15\times10^{-4}\,sec^{-1}$ for the chloropentaammine $3.63\times10^{-4}\,sec^{-1}$ for the bromopentaammine, and $1.1\times10^{-4}\,sec^{-1}$ for the iodopentaammine at 80°C. The energies of activation were 20 kcal/mol (chloropentaammine), 23 kcal/mol (bromopentaamine), and 30 kcal/mol (iodopentaammine). The reactions proceed through the following two steps:

$$[Ru(NH_3)_5X]^{2+} + H_2O \longrightarrow [Ru(NH_3)_5H_2O]^{3+} + X^-$$

$$[Ru(NH_3)_5H_2O]^{3+} + X^{*-} \longrightarrow [Ru(NH_3)_5X^*]^{2+} + H_2O$$

The first step is regarded as the rate-determining one.

There have been several investigations of the direct replacement of a halide ligand by a free halide ion in solutions of metal halides[1,2] and halogenoammine complexes[3,4]. In most instances of this type of isotopic replacement, especially with octahedral complexes, the rate of exchange has been found to be controlled by the rate of aquation of the complex. For halogenopentaammineruthenium(III) complexes, however, no research has been done, as far as we know.

The results of the present kinetic study were compared with the results for d^6-metal halogenopentaammines, and the mechanism of the isotopic exchange reaction was explained on the basis of the kinetic data.

Expermental

Reagents. All the chemicals used were of a reagent grade. The radio-isotopes, $^{36}Cl(HCl)$, $^{82}Br(NH_4Br)$, and $^{131}I(NaI)$, were obtained from the Japan Radioisotope Association, Tokyo, and were used as radioactive tracers. 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 neuralization of the acid with sodium hydroxide.

Halogenopentaammineruthenium(III) Complexes. The $[Ru(NH_3)_5X]X_2$ (X=Cl, Br, I) complexes were prepared by the method described by Allen.[5] One gram of ruthenium trichloride mono-hydrate was dissolved in distilled water (6 m*l*), and then hydrazine (85%, 10 m*l*) was added. The mixture was stirred for 17 hr at room temperature, and then filtered several times. To this filtrate, concentrated hydrohalogenic acid was added to make the solution strongly acidic. After this solution had been refluxed for three hours, the respective complexes were obtained. The complex was collected by filtration and washed with ethanol and ether. The final product was obtained by three recrystallizations from the distilled water.

Found: H, 5.08; N, 23.75%. Calcd for $[Ru(NH_3)_5Cl]Cl_2$: H, 5.13; N, 23.93%.

Found: H, 3.30; N, 16.48%. Calcd for $[Ru(NH_3)_5Br]Br_2$: H, 3.52; N, 16.44%.

Found: H, 2.50; N, 12.11%. Calcd for $[Ru(NH_3)_5I]I_2$: H, 2.65; N, 12.35%.

Kinetic Runs. A reaction vessel containing a solution of p-toluenesulfonic acid, sodium halide, and the respective halogenopentaammine complex was kept in a water bath at a constant temperature. A small amount of a solution of radioactive halide was added, and the exchange reaction was initiated. For the cases of the chloro- and the bromocomplex, aliquots of the reaction mixture were pipetted out at appropriate intervals and added to the ice-cooled silver nitrate solution. The free halide ion was precipitated as the silver halide. In the case of the iodocomplex, however, the decomposition of the complex was observed when the reaction mixture was added to the silver nitrate solution; therefore, we used an anion-exchange resin (Amberlite IR-4B) to collect free iodide ions.

In all cases, the supernatant containing the redioactive halogenopentaammine complex was separated and the radioactivity was measured.

The beta-activity of ^{36}Cl was measured by means of a G.M. counter while the gamma-activities of ^{83}Br and ^{131}I were measured by means of a well-type NaI(Tl) scintillation counter.

Results and Discussion

The recovery yields of the free halide ion in reaction solutions were determined, by a series of preliminary experiments, to be: Cl^-: 100%, Br^-: 98.5%, and I^-: 99.5%. Therefore, the exchange rates were calculated using these corrected values.

The reactions have been carried out for a period 8—10 times half-time, and the exchange rates were calculated by McKay's equations,[6] (1) and (2):

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

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

where *R*, 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 halogenopentaam-

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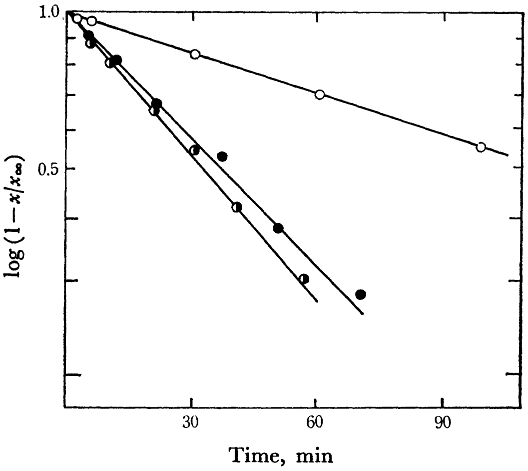

Fig. 1. Plots of $\log(1-x/x_\infty)$ *vs.* reaction time at 80°C.
●: Chloro-, ◑: Bromo-, ○: Iodocomplex.

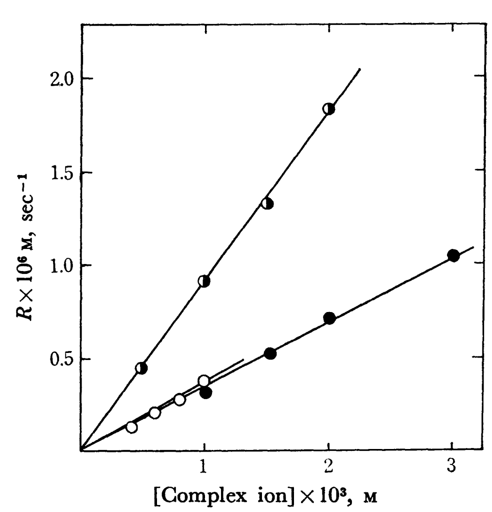

Fig. 2. Relationship between reaction rate (R) and complex-ion concentration.
●: Chlorocomplex, $[H^+]=1\times10^{-3}$ M, 80°C.
◑: Bromocomplex, $[H^+]=4\times10^{-3}$ M, 90°C.
○: Iodocomplex, $[H^+]=8\times10^{-3}$ M, 90°C.

mine complex at time t and at an infinite time. From Eq. (1), it can be expected that the plot of $\ln(1-X/X_\infty)$ *vs.* the reaction time will give a straight line with a slope of $-(a+b)R/ab$. From the plots in Fig. 1, the half-time of the exchange reaction was determined.

As is shown in Fig. 2, it is found that the exchange reaction is first-order with respect to the concentration of the complex.

As is shown in Fig. 3, there is no influence of the initial concentration of the halide ion on the reaction rate. This suggests that the bond formation between the halide and complex ion is not connected with rate-determining step in the exchange reaction.

No influence of the hydrogen ion on the reaction rate was observed under the present experimental conditions, as is shown in Fig. 4. Thus, the reaction rate, R, and rate constant, k_{ex}, can be expressed as follows:

$$R = k_{ex}[\text{complex}] \tag{3}$$

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

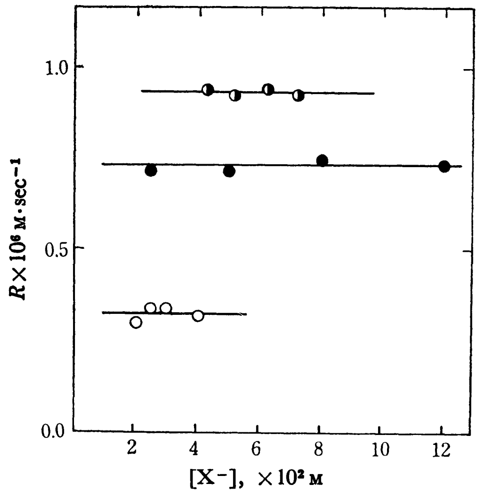

Fig. 3. Effects of halide-ion concentration on the rate
●: Chlorocomplex, $[H^+]=1\times10^{-3}$ M, 80°C.
◑: Bromocomplex, $[H^+]=4\times10^{-3}$ M, 90°C.
○: Iodocomplex, $[H^+]=8\times10^{-3}$ M, 90°C.

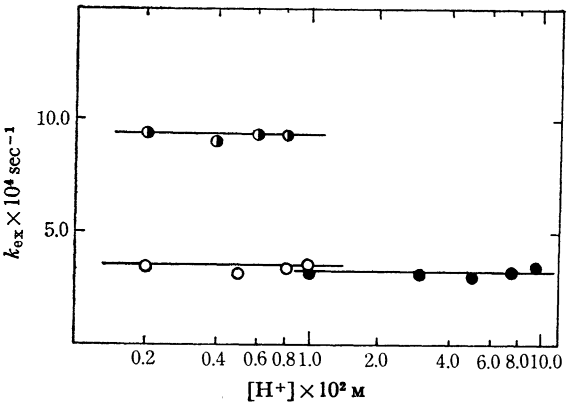

Fig. 4. Effects of hydrogen-ion concentration on the rate constants.
●: Chlorocomplex, ◑: Bromocomplex, ○: Iodocomplex

To know the dependence of the rate on the ionic strength, experiments were carried out while varying the ionic strength of the aqueous solution from 0.04 to 0.4 using sodium *p*-toluenesulfonate. The results are shown in Fig. 5. No practical effect of the ionic strength on the rate is found, this fact suggests that the charged species do not participate in the rate-determining process.

Figure 6 shows the Arrhenius plots, while the activation energies are listed, along with those of analogous and reference reactions, in Table 1.

The values of the rate constants of the exchange reactions are nearly the same as those of the acid-hydrolysis reactions. The values of both activation energies are also the same in the two kinds of the reactions except in the case of the iodopentaammine. From these facts, it may be concluded that the exchange reaction proceeds through the aquation process (5), and that the anation reaction (6) follows. The former step is presumably the rate-determining one.

$$[Ru(NH_3)_5X]^{2+} + H_2O = [Ru(NH_3)_5H_2O]^{3+} + X^- \tag{5}$$

$$[Ru(NH_3)_5H_2O]^{3+} + X^{*-} = [Ru(NH_3)_5X^*]^{2+} + H_2O \tag{6}$$

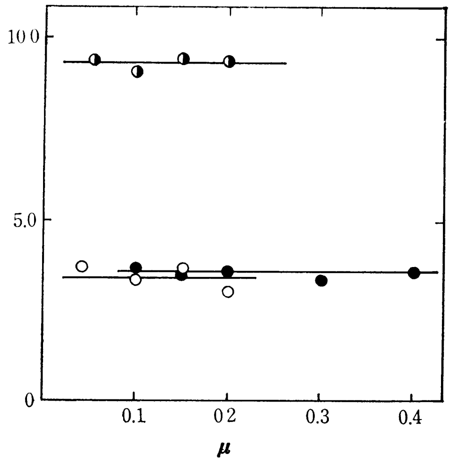

Fig. 5. Dependence of ionic strength on the rate constant.
●: Chloro-, ◑: Bromo-, ○: Iodocomplex

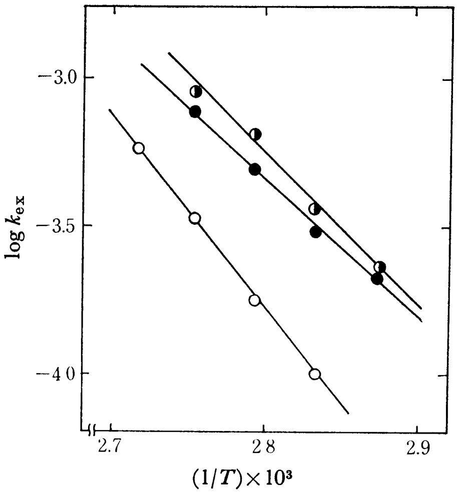

Fig. 6. Arrhenius plots for isotopic ligand exchange reactions.
●: Chloro-, ◑: Bromo-, ○: Iodocomplex

TABLE 1. RATES AND ACTIVATION ENERGIES OF ISOTOPIC LIGAND EXCHANGE REACTIONS OF $[M(NH_3)_5X]$ COMPLEXES

Complex	k_{ex}[a] 10^{-4} sec^{-1}	E_a kcal mol^{-1}	k[b] 10^{-4} sec^{-1}
$[Ru(NH_3)_5Cl]^{2+}$	3.15	20.0±0.5	3.28[c]
$[Ru(NH_3)_5Br]^{2+}$	3.63	23.2±0.9	3.99[f]
$[Ru(NH_3)_5I]^{2+}$	1.1	30 ±1	1.64[f]
$[Rh(NH_3)_5Cl]^{2+}$	0.32[e]	21	
$[Rh(NH_3)_5Br]^{2+}$	0.278[d]	24	
$[Rh(NH_3)_5I]^{2+}$	0.070[e]	26	
$[Ir(NH_3)_5Cl]^{2+}$	0.0048[e]	23	
$[Ir(NH_3)_5Br]^{2+}$	0.0047[d]	23	
$[Ir(NH_3)_5I]^{2+}$	0.0017[e]	26	

a) Temperature 80°C, ionic strength $\mu=0.1$.
b) Rate constants for acid hydrolyses at 80.1°C.
c) from Ref. 4.
d) from Ref. 3.
e) from Ref. 7.
f) from Ref. 8.

As the exchanging group is varied from chloride to bromide or iodide, the exchange rates are found to be in the order; Br>Cl>I for the halogenopentaammineruthenium(III) complexes. Similar trends have been found by Schmidt[4] for the halide-ion exchange rates of rhodium(III) and iridium(III) pentaammines.

If the mechansim for the aquation reaction (5) were of the dissociative (S_N1 lim) type, then the iodocomplex would be expected to be faster than the others. The present slower rate may be attributed to the higher activation energy term (Table 1) and indicates that bond breaking alone is not of major importance in Reaction (5).

A soft base such as an iodide ion tends to make a covalent bond, and the effective charge of the central metal may be decreased. If Reaction (5) proceeds through an S_N2 path, the exchange rate increases with an increase in the effective charge of the central metal ion.

Broomhead and Maguire[8] cited the ideas of Pearson and Songstad[9] to interpret their experimental results on the hydrolysis of analogous complexes. The replacement of the hard base, H_2O, by bases such as Cl^-, Br^-, or I^-, where the hardness is decreasing, should lead to a destabilization of the transition state in an S_N2 process and, consequently, to a slower reaction with a high E_a value. The slower rate and the higher activation energy for the iodocomplex are in good agreement with the predictions, assuming the presence of an S_N2 mechanism.

As is shown in Table 1, the exchange rate constants, k_{ex}, are generally smaller than those of acid hydrolyses. This would seem to suggest that Reaction (6) may be partly concerned with the over-all reaction rate; however, these differences are too small for another reaction mechanism to be considered.

Table 1 shows the isotopic exchange reaction rates of the three metal complexes for comparative purposes. It can be seen that the relative rate constants for the isotopic ligand exchange at 80°C are Ru(III)> Rh(III)>Ir(III) for all the halogenopentaammine complexes. This order is also in agreement with that predicted from the crystal-field consideration by Broomhead *et al.*,[7] assuming a seven-coordinated intermediate in an acid hydrolysis reaction corresponding to Eq. (5).

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