Studies of the Ruthenium Complexes. XI.[1] The Reaction Mechanism of the Base Hydrolysis of Halogenopentaammineruthenium(III) Complexes[2]

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(Received June 9, 1975)

The base hydrolysis of halogenopentaammineruthenium(III) complexes, $[RuX(NH_3)_5]X$, (X=Cl, Br, and I), has been studied in a solution with a 0.03—0.2 M hydroxide ion concentration in order to clarify the reaction mechanism. Some deviations from the first-order rate plots were observed early in the reaction. By the analysis of these results, it was proved that the concentration change with time for each species participating in the reaction was expressed by a linear combination of two exponential functions. The reaction can be well accounted for by a mechanism involving S_N2 CB and S_N2 processes:

$$[RuX(NH_3)_5]^{2+} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [RuX(NH_3)_4(NH_2)]^+ + H_2O$$

$$[RuX(NH_3)_4(NH_2)]^+ + OH^- \xrightarrow[H_2O]{k_2} [Ru(OH)(NH_3)_5]^{2+} + X^- + OH^-$$

$$[RuX(NH_3)_5]^{2+} + OH^- \xrightarrow{k_3} [Ru(OH)(NH_3)_5]^{2+} + X^-$$

The rate constants, k_1, k_{-1}, k_2, and k_3, at 15 °C were determined to be 9.29×10^{-2} $M^{-1}\,s^{-1}$, 2.65×10^{-2} s^{-1}, 6.78×10^{-1} $M^{-1}\,s^{-1}$, and 1.13×10^{-1} $M^{-1}\,s^{-1}$ respectively for the chloropentaammine complex.

Among the several investigations[3-10] of the base hydrolysis of the metal-ammine complexes, Broomhead and his co-workers[9,10] have reported that the reaction of the halogenopentaammineruthenium(III) complex proceeds *via* the S_N1 conjugated-base (S_N1 CB) mechanism in a solution with a 3.78×10^{-4}—2.65×10^{-3} M hydroxide ion concentration. Certainly, this interpretation is reasonable. However, other mechanisms are possible considering the strong affinity of the ruthenium(III) ion for the oxygen atom. Thus, the base hydrolysis of halogenopentaammineruthenium(III) complexes, $[RuX(NH_3)_5]^{2+}$, X=Cl, Br, and I, has been studied at high concentrations of hydroxide ions (from 0.03 M to 0.2 M). On the basis of the experimental results, we assumed three types of elementary reactions for the mechanism and examined their validities by means of computer-simulation analysis.

Experimental

Preparation of Complexes. The complexes, $[RuX(NH_3)_5](ClO_4)_2$, were prepared by the method of the literature.[9] The complexes were confirmed by elemental analysis and by the visible and UV spectra. Found: H, 3.47; N, 16.32%. Calcd for $[RuCl(NH_3)_5](ClO_4)_2$: H, 3.60; N, 16.65%. Found: H, 3.40; N, 14.49%. Calcd for $[RuBr(NH_3)_5](ClO_4)_2$: H, 3.25; N, 15.06%. Found: H, 2.87; N, 13.58%. Calcd for $[RuI(NH_3)_5](ClO_4)_2$: H, 2.95; N, 13.68%.

Kinetic Run. The reaction solutions were adjusted to the ionic strength of 1.0 M and the hydroxide-ion concentration of 0.03—0.2 M with sodium hydroxide and sodium perchlorate. The reaction temperature was kept constant within ±0.1 °C by circulating water from a thermostated bath. A change in the concentration of $[RuX(NH_3)_5]^{2+}$ (or $[Ru(OH)(NH_3)_5]^{2+}$) as a function of time was followed by measuring the absorbance at λ_{max} of the spectra of the respective complexes, using a Hitachi 124 recording spectrophotometer.

Results and Discussion

The changes in the spectra during the base hydrolysis of bromopentaammine are shown in Fig. 1. The absorption band (398 nm) of the original complex rapidly decreases, with a slight shift to the low-wavelength region, and a new peak appears at about 300 nm. This peak grows with the shift to a constant wavelength (298 nm), a tendency which is in agreement with that of the hydroxo-complex.[9] Similar results were observed in the base hydrolysis of the other two complexes.

As is shown in Fig. 2, some deviations from the straight lines of the first-order plots are observed in the initial period of the reaction. This fact can be interpreted by assuming that the measured absorbance involves that of a short-lived intermediate in addition to that of the reactant. If the intermediate is an amido-

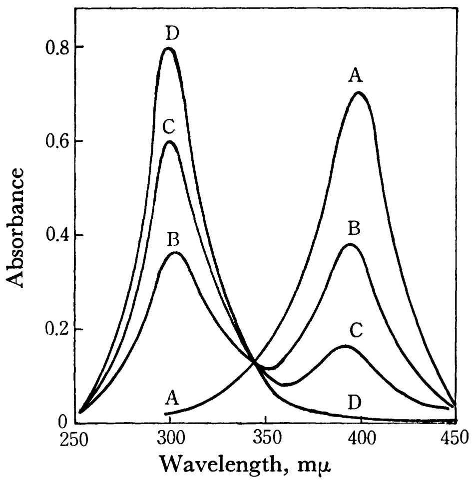

Fig. 1. Spectral changes during the base hydrolysis of $[RuBr(NH_3)_5]^{2+}$.
$[OH^-]$: 0.03 M, μ=1.0, Temp.=10.0 °C.
A; initial B; 30 s C; 60 s D; final (250 s)

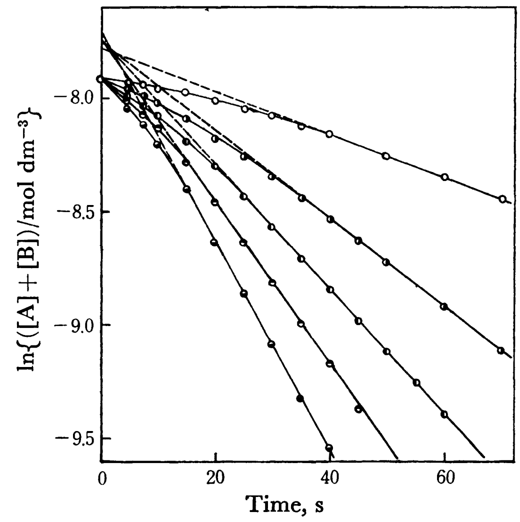

Fig. 2. Plots of ln ([A]+[B]) *vs.* reaction time.
A: $[RuBr(NH_3)_5]^{2+}$, B: $[RuBr(NH_3)_4(NH_2)]^+$.

complex, which is a conjugated base of the reactant, it may be acceptable that the values of λ_{max} and the extinction coefficient of the intermediate are nearly equal to those of the reactant.

Thus, we assumed the following three types of elementary reactions:

Mechanism I (S_N1 CB):

$$[RuX(NH_3)_5]^{2+} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [RuX(NH_3)_4(NH_2)]^+ + H_2O \quad (1)$$

$$[RuX(NH_3)_4(NH_2)]^+ \xrightarrow{k_2} [Ru(NH_3)_4(NH_2)]^{2+} + X^- \quad (2)$$

$$[Ru(NH_3)_4(NH_2)]^{2+} + H_2O \xrightarrow{\text{fast}} [Ru(OH)(NH_3)_5]^{2+} \quad (3)$$

$$[A] = \{(\lambda_1-k'_{-1}-k_2)e^{-\lambda_1 t}-(\lambda_2-k'_{-1}-k_2)e^{-\lambda_2 t}\}[A]_0/(\lambda_1-\lambda_2) \quad (4)$$

$$[B] = (-e^{-\lambda_1 t}+e^{-\lambda_2 t})k_1'[A]_0/(\lambda_1-\lambda_2) \quad (5)$$

$$[A] + [B] = \{(\lambda_1-p)e^{-\lambda_1 t}-(\lambda_2-p)e^{-\lambda_2 t}\}[A]_0/(\lambda_1-\lambda_2) \quad (6)$$

where $[A] = [RuX(NH_3)_5]^{2+}$, $[B] = [RuX(NH_3)_4(NH_2)]^+$, $\lambda_1=(p+\sqrt{p^2-4q})/2$, $\lambda_2=(p-\sqrt{p^2-4q})/2$, $p=k_1'+k_{-1}'+k_2$, $q=k_1'k_2$, $k_1'=k_1[OH^-]$, and $k_{-1}'=k_{-1}[H_2O]$. The zero subscript indicates the initial concentration.

Mechanism II (CB and S_N2):

$$[RuX(NH_3)_5]^{2+} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [RuX(NH_3)_4(NH_2)]^+ + H_2O \quad (7)$$

$$[RuX(NH_3)_5]^{2+} + OH^- \xrightarrow{k_2} [Ru(OH)(NH_3)_5]^{2+} + X^- \quad (8)$$

$$[A] = \{(\lambda_1-k'_{-1})e^{-\lambda_1 t}-(\lambda_2-k'_{-1})e^{-\lambda_2 t}\}[A]_0/(\lambda_1-\lambda_2) \quad (9)$$

$$[B] = (-e^{-\lambda_1 t}+e^{-\lambda_2 t})k_1'[A]_0/(\lambda_1-\lambda_2) \quad (10)$$

$$[A] + [B] = \{(\lambda_1-k_1'-k'_{-1})e^{-\lambda_1 t} -(\lambda_2-k_1'-k'_{-1})e^{-\lambda_2 t}\}[A]_0/(\lambda_1-\lambda_2) \quad (11)$$

where $p=k_1'+k_{-1}'+k_2'$, $q=k_{-1}'k_2'$, and $k_2'=k_2[OH^-]$. The other notations are the same as those for Mechanism I.

Mechanism III (S_N2 CB and S_N2):

$$[RuX(NH_3)_5]^{2+} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [RuX(NH_3)_4(NH_2)]^+ + H_2O \quad (12)$$

$$[RuX(NH_3)_4(NH_2)]^+ + OH^- \xrightarrow[H_2O]{k_2} [Ru(OH)(NH_3)_5]^{2+} + X^- + OH^- \quad (13)$$

$$[RuX(NH_3)_5]^{2+} + OH^- \xrightarrow{k_3} [Ru(OH)(NH_3)_5]^{2+} + X^- \quad (14)$$

$$[A] = \{(k_1'+k_3'-\lambda_2)e^{-\lambda_1 t}-(k_1'+k_3'-\lambda_1)e^{-\lambda_2 t}\}[A]_0/(\lambda-\lambda_2) \quad (15)$$

$$[B] = (-e^{-\lambda_1 t}+e^{-\lambda_2 t})k_1'[A]_0/(\lambda_1-\lambda_2) \quad (16)$$

$$[A] + [B] = \{(k_3'-\lambda_2)e^{-\lambda_1 t}-(k_3'-\lambda_1)e^{-\lambda_2 t}\}[A]_0/(\lambda_1-\lambda_2) \quad (17)$$

where $p=k_1'+k_{-1}'+k_2'+k_3'$, $q=k_1'k_2'+k_{-1}'k_3'+k_2'k_3'$, $k_2'=k_2[OH^-]$, and $k_3'=k_3[OH^-]$.

For all the mechanisms, [A]+[B] is expressed by Eq. 18:

$$[A] + [B] = C_1e^{-\lambda_1 t} + C_2e^{-\lambda_2 t} \quad (18)$$

Where C_1 and C_2 are the constants.

In the stationary-state period, the first term on the right-hand of Eq. 18 is nearly equal to zero. Therefore we can obtain the λ_2 value from the plots of ln{([A]+[B])} *vs.* the time. The values of λ_2 and λ_1 correspond to the respective slopes of the straight lines in Figs. 2 and 3. As $-\lambda_1$ and $-\lambda_2$ are roots of the quadratic equation, $\lambda_1+\lambda_2$ and $\lambda_1 \cdot \lambda_2$ are equal to p and q respectively. Plots of $(\lambda_1+\lambda_2)$ (=p) and $\lambda_1 \cdot \lambda_2$ (=q) *vs.* the concentration of hydroxide ions are shown in Fig. 4.

Let us examine the validity of the reaction mechanisms. For Mechanism I, k_1' has a linear dependence on the concentration of hydroxide ions, and the plot of p *vs.* the hydroxide-ion concentration should be a straight line, with an intercept corresponding to $(k_{-1}+$

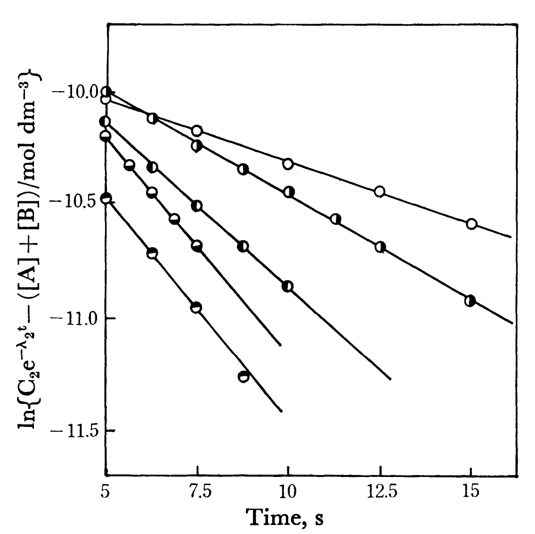

Fig. 3. Plots of ln{$C_2e^{-\lambda_2 t}$−([A]+[B])} *vs.* reaction time.
A: $[RuBr(NH_3)_5]^{2+}$, B: $[RuBr(NH_3)_4(NH_2)]^+$.
$[OH^-]$; -○- 0.03 M, -◑- 0.07 M, -◐- 0.11 M, -◒- 0.16 M, -◓- 0.20 M.

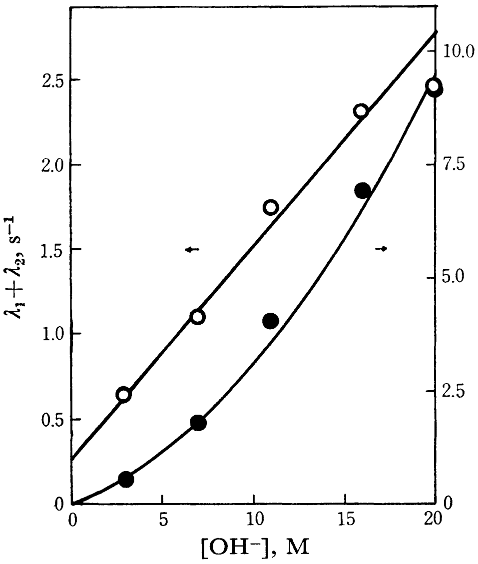

Fig. 4. Plots of $\lambda_1+\lambda_2$ and $\lambda_1\cdot\lambda_2$ *vs.* [OH$^-$].

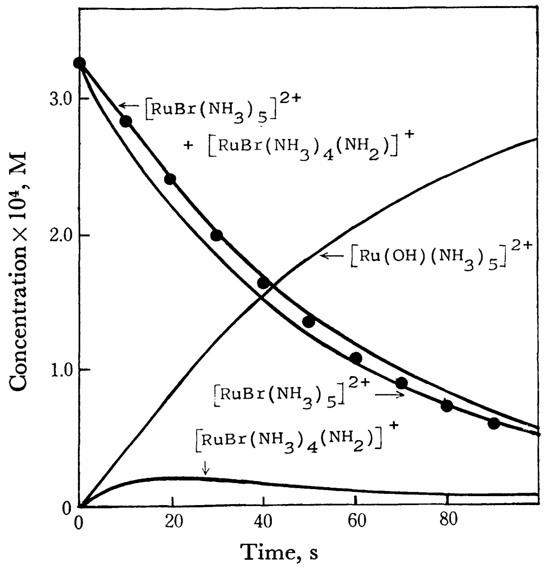

Fig. 5. Concentration variation of chemical species participating in the base hydrolysis of chloropentaammineruthenium(III).
$[RuCl(NH_3)_5]_0^{2+}=3.267\times10^{-4}$ M, [OH$^-$]$=0.11$ M, Temp.$=15.0$ °C, $\mu=1.0$ mol·kg^{-1}, k_1, k_2, k_3, and k'_{-1} are 9.29×10^{-2} M^{-1} s^{-1}, 6.78×10^{-1} M^{-1} s^{-1}, 1.13×10^{-1} M^{-1} s^{-1}, and 2.65×10^{-2} s^{-1} respectively.
●, Experimental; ——, Simulation.

k_2). Just as in the case of Mechanism I, a linear relationship can be expected to hold for Mechanisms II and III. Plots of q *vs.* the concentration of hydroxide ions should be straight lines for Mechanisms I and II, while a quadratic curve can be expected for Mechanism III; that is, the types of curves for Mechanisms II and III should be different. The former has the same double real roots, but the latter, two different real roots.

Judging from Fig. 4, the relation is not linear but quadratic, and the curve favors Mechanism III. Especially, if the reaction proceeds by means of Mechanism I, no irregularities should be allowed in the initial stage of the reaction.

Table 1. Rate constants and kinetic parameters of the base hydrolysis for chloropentaammineruthenium(III) complex

	Rate constants (Temp., °C)	Frequency factor, A, s^{-1}	E_a (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)	$\Delta H^{\ddagger}$ (kcal/mol)
k_1, 10^{-2}·M^{-1}·s^{-1}	2.4 ±0.2 (3.0)	3.1×10^{12}	18	−3.3	17
	3.4 ±0.3 (6.0)				
	5 ±1 (10.0)				
	9 ±2 (15.0)				
	14 ±5 (19.0)				
k_{-1}, 10^{-2}·s^{-1}	2.01±0.08 (3.0)	1.5×10^{10}	3.6	−55	3.1
	2.2 ±0.1 (6.0)				
	2.4 ±0.6 (10.0)				
	2.7 ±0.3 (15.0)				
	2.9 ±0.5 (19.0)				
k_2, 10^{-2}·M^{-1}·s^{-1}	8.5 ±0.4 (3.0)	4.3×10^{20}	27	34	27
	14.5 ±0.5 (6.0)				
	29 ±1 (10.0)				
	68 ±5 (15.0)				
	131 ±9 (19.0)				
k_3, 10^{-2}·M^{-1}·s^{-1}	2.1 ±0.8 (3.0)	6.9×10^{15}	22	12	22
	3.2 ±0.2 (6.0)				
	5.9 ±0.4 (10.0)				
	11 ±2 (15.0)				
	19 ±3 (19.0)				
k_{obsd}, 10^{-2}·M^{-1}·s^{-1}	2.7 ±0.1 (3.0)	1.1×10^{22}	30	40	29
	4.9 ±0.1 (6.0)				
	9.4 ±0.5 (10.0)				
	26 ±2 (15.0)				
	52 ±4 (19.0)				

Table 2. Rate constants and kinetic parameters of the base hydrolysis for bromopentaammineruthenium(III) complex

	Rate constants (Temp., °C)	Frequency factor, A, s^{-1}	E_a (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)	$\Delta H^{\ddagger}$ (kcal/mol)
k_1, $10^{-2}\cdot M^{-1}\cdot s^{-1}$	1.18±0.08 (3.0)	6.6×10^{28}	39	11	38
	2.5 ±0.2 (6.0)				
	7 ±1 (10.0)				
	23 ±6 (15.0)				
	57 ±9 (19.0)				
k_{-1}, $10^{-2}\cdot s^{-1}$	1.48±0.06 (3.0)	2.6×10^{8}	13	−22	12
	1.9 ±0.1 (6.0)				
	2.7 ±0.1 (10.0)				
	4.0 ±0.6 (15.0)				
	5.4 ±0.7 (19.0)				
k_2, $10^{-2}\cdot M^{-1}\cdot s^{-1}$	21.6 ±0.6 (3.0)	1.1×10^{12}	16	−5.3	16
	29.6 ±0.8 (6.0)				
	44 ±2 (10.0)				
	73 ±7 (15.0)				
	107 ±9 (19.0)				
k_3, $10^{-2}\cdot M^{-1}\cdot s^{-1}$	2.0 ±0.3 (3.0)	2.6×10^{19}	27	29	26
	3.0 ±0.3 (6.0)				
	6.7 ±0.4 (10.0)				
	15 ±2 (15.0)				
	28 ±4 (19.0)				
k_{obsd}, $10^{-2}\cdot M^{-1}\cdot s^{-1}$	3.0 ±0.2 (3.0)	1.4×10^{19}	26	27	26
	5.8 ±0.5 (6.0)				
	12.0 ±0.9 (10.0)				
	22 ±4 (15.0)				
	44 ±3 (19.0)				

Table 3. Rate constants and kinetic parameters of the base hydrolysis for iodopentaammineruthenium(III) complex

	Rate constants (Temp., °C)	Frequency factor, A, s^{-1}	E_a (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)	$\Delta H^{\ddagger}$ (kcal/mol)
k_1, $10^{-2}\cdot M^{-1}\cdot s^{-1}$	0.33±0.04 (3.0)	6.1×10^{37}	51	113	50
	0.70±0.06 (6.0)				
	3.3 ±0.7 (10.0)				
	16 ±3 (15.0)				
	53 ±4 (19.0)				
k_{-1}, $10^{-2}\cdot s^{-1}$	1.18±0.09 (3.0)	9.5×10^{7}	13	−24	12
	1.5 ±0.1 (6.0)				
	2.2 ±0.2 (10.0)				
	2.7 ±0.2 (15.0)				
	4.4 ±0.4 (19.0)				
k_2, $10^{-2}\cdot M^{-1}\cdot s^{-1}$	32 ±1 (3.0)	1.3×10^{2}	3.3	−51	2.7
	35 ±2 (6.0)				
	38 ±2 (10.0)				
	42 ±3 (15.0)				
	45 ±4 (19.0)				
k_3, $10^{-2}\cdot M^{-1}\cdot s^{-1}$	1.2 ±0.1 (3.0)	2.9×10^{18}	26	24	25
	1.9 ±0.2 (6.0)				
	4.1 ±0.4 (10.0)				
	9.3 ±0.3 (15.0)				
	15 ±1 (19.0)				
k_{obsd}, $10^{-2}\cdot M^{-1}\cdot s^{-1}$	2.7 ±0.03 (3.0)	5.8×10^{18}	26	25	25
	3.05±0.06 (6.0)				
	7.0 ±0.2 (10.0)				
	19.5 ±0.3 (15.0)				
	38 ±3 (19.0)				

Now, let us estimate the rate constants based on Mechanism III. In Fig. 4, the slope and intercept of the straight line indicate $(k_1+k_2+k_3)$ and k_{-1} respectively. Since the variation in the concentration $(=\{[A]+[B]\})$ is almost linear in the initial stage of the reaction, as is shown in Fig. 5, the k_3 value can be obtained from the slope of the initial line. The values of k_1 and k_2 are calculated by the relation of p and q. Thus, all the rate constants were determined; they are given in Tables 1—3. It seems that the dissociation of hydrogen is very difficult in comparison with the hydrogen-exchange reaction of the hexaammineruthenium(III) complex.[10)]

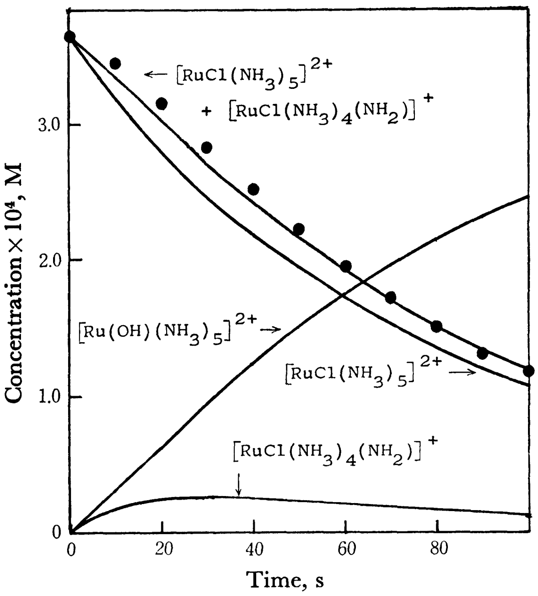

Fig. 6. Concentration variation of chemical species participating in the base hydrolysis of bromopentaammineruthenium(III).
$[RuBr(NH_3)_5]_0^{2+}=3.654\times10^{-4}$ M, $[OH^-]=0.11$ M, Temp. = 10.0 °C, $\mu=1.0$ mol kg^{-1}, k_1, k_2, k_3, and k'_{-1} are 6.79×10^{-2} M^{-1} s^{-1}, 4.46×10^{-1} M^{-1} s^{-1}, 6.74×10^{-2} M^{-1} s^{-1} and 2.65×10^{-2} s^{-1} respectively.
● Experimental; —— Simulation.

Finally, we carried out a simulation analysis based on Eqs. 15—17 in order to check the validity of the estimated rate constants. The calculated results are shown in Figs. 5 and 6. The concentration of $[Ru(OH)(NH_3)_5]^{2+}$ was calculated by means of $([A]_0-[A]-[B])$. The curves showing the concentration change with the reaction time for the original and intermediate complexes obtained from the simulative calculation are in agreement with the experimental results.

As has already been pointed out[11)] in connection with the influence of hydrogen peroxide on the reaction rate of the base hydrolysis of metal ammine complexes, the rate constant decreases upon the addition of hydrogen peroxide for the base hydrolysis with the S_N1 CB mechanism, while it increases for the reaction process of the S_N2 mechanism.

In the present experiment on the base hydrolysis, the rate constant in the solution of each 0.11 M hydroxide ion and hydrogen peroxide is about three times larger than that in the 0.11 M hydroxide ion solution. This fact indicates that the S_N2 mechanism favors the base hydrolysis reaction of halogenopentaammineruthenium(III).

The calculations were performed on a FACOM 230–25 computer at the Engineering Research Center of Kumamoto University.

The authors wish to thank the Ministry of Education for the financial support (No. 847009) granted to this research.

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