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KINETICS AND MECHANISM ON THE AQUATION AND ANATION REACTIONS OF MONOCHLOROACETATOPENTAAMMINERUTHENIUM(III) COMPLEX IN AQUEOUS SOLUTION

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The aquation and anation reactions of monochloroacetatopentaammineruthenium(III) complex are studied to know the elementary reaction mechanism under the same reaction conditions. The aquation reaction seems to take the S_N 2 mechanism, through the process which involves the seven-coordinated intermediate while the anation reaction is well illustrated by the limiting S_N 1 mechanism. The elementary rate constants for the anation reaction was determined.

Some studies on the anation reactions of Co(III) complexes[1,2] have been made to clarify the elementary reaction mechanism. It is difficult to evaluate the backward reaction in an ordinary aquation reaction. In this experiment, the rates of aquation and anation reactions were determined in the solution with various ligand ion concentrations. All the reactions were carried out in the solution of the constant acidity (pH 2.0) and ionic strength(μ 1.00) adjusted with p-toluenesulfonic acid, monochloroacetic acid, and sodium hydroxide. Monochloroacetatopentaammineruthenium(III) and aquopentaammineruthenium(III) complexes were prepared by the method described in literatures[3,4]. A Shimadzu UV 200 recording spectrophotometer was used to measure absorption spectrum of monochloroacetatopentaammineruthenium(III) complex. The details of the experiment have already been reported[5].

If we assume that the aquation and anation reaction proceed through an elementary process which involves a five- or seven-coordinated intermediate, the reaction mechanism can be expressed as follows:

Mechanism I (Five-coordinated intermediate).

$$[RuX(NH_3)_5]^{2+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Ru(NH_3)_5]^{3+} + X^- \tag{1}$$

$$[Ru(NH_3)_5]^{3+} + H_2O \underset{k_4}{\overset{k_3}{\rightleftharpoons}} [Ru(OH_2)(NH_3)_5]^{3+} \tag{2}$$

$$k_{obs} = (k_1k_3' + k_2k_4[X^-])/(k_2[X^-] + k_3') \tag{3}$$

Mechanism II (Seven-coordinated intermediate).

$$[RuX(NH_3)_5]^{2+} + H_2O \underset{k_6}{\overset{k_5}{\rightleftharpoons}} [RuX(OH_2)(NH_3)_5]^{2+} \tag{4}$$

$$[\mathrm{RuX(OH_2)(NH_3)_5}]^{2+} \underset{k_8}{\overset{k_7}{\rightleftharpoons}} [\mathrm{Ru(OH_2)(NH_3)_5}]^{3+} + \mathrm{X}^- \qquad (5)$$

$$k_{obs} = (k_5'k_7 + k_6k_8[\mathrm{X}^-])/(k_6 + k_7) \qquad (6)$$

where X^- is monochloroacetate ion, $k_1 \sim k_8$ denote the rate constant for the respective elementary process, and k_3' and k_5' are pseudo-first-order rate constants. The observed rate constant, k_{obs}, is derived from the steady-state approximation of the intermediate.

As is shown in Fig.1. the linear relationship between the k_{obs} and $[\mathrm{X}^-]$ for the aquation reaction can be well elucidated by the Eq.6, and then the aquation reaction proceeds taking the seven-coordinated intermediate. The similar analysis can be used on the anation reaction. Plots of k_{obs} vs. $[\mathrm{X}^-]$ in Fig.1 show gentle curves which can be fitted to the Eq.3. The intermediate of the anation reaction will be deduced to be five-coordinated complex.

If the aquation and anation reactions can be expressed by the same mechanism, k_{obs} for the former and the latter must be identical under the same reaction conditions. However, both of them are not identical, so it is evident that two reactions pass through the different mechanisms.

The Equation 3 can be reformed as follows:

$$1/(k_4 - k_{obs}) = 1/(k_4 - k_1) + k_2[\mathrm{X}^-]/(k_4 - k_1)k_3' \qquad (3')$$

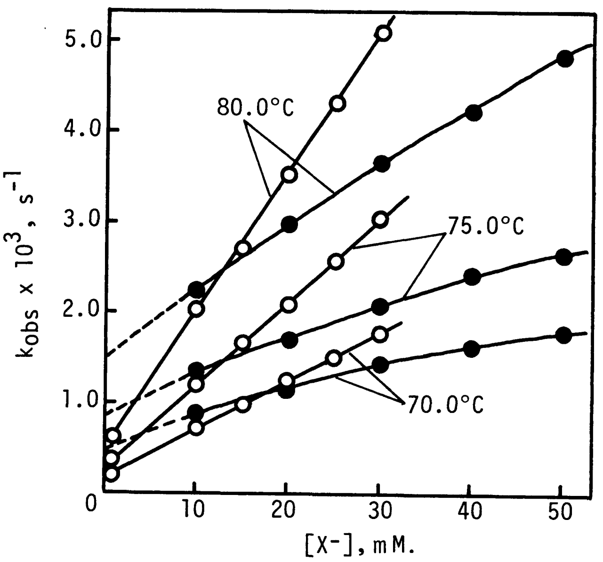

Fig.1. Plots of k_{obs} vs. $[\mathrm{X}^-]$.
-o- Aquation; -●- Anation; pH=2.0; μ=1.00.

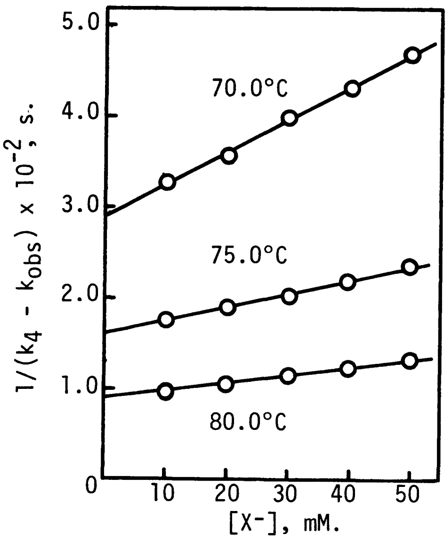

Fig.2. Plots of $1/(k_4 - k_{obs})$ vs. $[\mathrm{X}^-]$.

The values of k_1 is obtained by extrapolating the curves in Fig.1. The rough values of k_4 were evaluated graphically from the value at $[\mathrm{X}^-] \to \infty$, and then the accurate values were calculated by means of repeating least square-error method based on the Eq.3! The results of calculations are shown in Fig.2 and Table 1. The intercept and the slope of the straight line in Fig.2 indicate the values of $1/(k_4 - k_1)$ and $k_2/(k_4 - k_1)k_3'$ respectively.

From the Eqs.1 and 2, the linear differential equations are described as follows:

$$d([RuX(NH_3)_5]^{2+})/dt = -k_1([RuX(NH_3)_5]^{2+}) + k_2[X^-]([Ru(NH_3)_5]^{3+}) \quad (7a)$$

$$d([Ru(NH_3)_5]^{3+})/dt = k_1([RuX(NH_3)_5]^{2+}) + k_4([Ru(OH_2)(NH_3)_5]^{3+})$$
$$- (k_2[X^-] + k_3')([Ru(NH_3)_5]^{3+}) \quad (7b)$$

$$d([Ru(OH_2)(NH_3)_5]^{3+})/dt = k_3'([Ru(NH_3)_5]^{3+}) - k_4([Ru(OH_2)(NH_3)_5]^{3+}) \quad (7c)$$

The time dependence of $[RuX(NH_3)_5]^{2+}$, $[Ru(NH_3)_5]^{3+}$, and $[Ru(OH_2)(NH_3)_5]^{3+}$ concentration was respectively derived from Eqs.7a~c.

$$[RuX(NH_3)_5]^{2+} = ([Ru(OH_2)(NH_3)_5]^{3+})_0 k_2[X^-]k_4\{\lambda_2 e^{-\lambda_1 t}-\lambda_1 e^{-\lambda_2 t}+(\lambda_1-\lambda_2)\}$$
$$/(\lambda_1-\lambda_2)\beta \quad (8a)$$

$$[Ru(NH_3)_5]^{3+} = ([Ru(OH_2)(NH_3)_5]^{3+})_0 k_4\{-(\lambda_2 k_1+\beta)e^{-\lambda_1 t}+(\lambda_1 k_1+\beta)e^{-\lambda_2 t}$$
$$+(\lambda_1-\lambda_2)k_1\}/(\lambda_1-\lambda_2)\beta \quad (8b)$$

$$[Ru)OH_2)(NH_3)_5]^{3+} = ([Ru(OH_2)(NH_3)_5]^{3+})_0[\{\lambda_2(k_1k_3'-\beta)+\beta k_4\}e^{-\lambda_1 t}$$
$$-\{\lambda_1(k_1k_3'-\beta)+\beta k_4\}e^{-\lambda_2 t}+(\lambda_1-\lambda_2)k_1k_3']/(\lambda_1-\lambda_2)\beta \quad (8c)$$

where $\lambda_1 = \alpha-\sqrt{\alpha^2-\beta}$; $\lambda_2 = \alpha+\sqrt{\alpha^2-\beta}$; $\alpha = (k_1+k_2[X^-]+k_3'+k_4)/2$; $\beta = k_1k_3'+k_1k_4+k_2[X^-]k_4$; the subscript zero denotes the initial concentration.

The values of k_1, k_4 and k_2/k_3' are already estimated, however, the values of k_2 and k_3' are unknown. When the k_3' value is assumed arbitrarily to be 1.00 s^{-1} under the reaction conditions of temperature = 70.0°C, $[X^-]$ = 10mM, pH =2.0 and μ = 1.00, the k_2 value is determined to be 12.4 $M^{-1}s^{-1}$ from the value of k_2/k_3' (see Table 1).

Table 1. Kinetic Rate Constants and Activation Parameters.

Temp.°C	Aquation		Anation		
	$k_f \times 10^4$	$k_b \times 10^2$	$k_1 \times 10^3$	$k_4 \times 10^3$	k_2/k_3'
70.0	1.97	5.25	4.60	3.89	12.40
75.0	3.31	8.95	8.30	7.10	9.37
80.0	5.10	15.20	14.70	12.60	9.35

	A	Ea,kcal/mol	$\Delta S^{\ddagger}$,e.u.	$\Delta H^{\ddagger}$,kcal/mol
k_f	4.01×10^{10}	22.5	-12.32	21.8
k_b	1.06×10^{15}	25.6	7.92	24.9
k_1	3.03×10^{14}	28.0	5.43	27.3
k_4	4.14×10^{15}	28.3	10.63	27.6

k_f, k_1, and k_4: First-order rate constants in s^{-1} unit. k_3': Pseudo first-order rate constant in s^{-1} unit. k_b and k_2: Second-order rate constant in $M^{-1}s^{-1}$ unit. Reaction conditions are the same as those in Fig.1.

Here, an attempt was carried out to justify the estimation of the kinetic rate constant for each elementary reaction. The time-conversion curve of concentration for each complex species was prepared by the calculation from Eqs. 8a~c using the tentative value of the rate constant given in Table 1. As is shown in Fig.3, the time conversion curve for the initial complex, $[RuX(NH_3)_5]^{2+}$, obtained from the simulative calculation is in agreement with the experimental determination. The concentration of the intermediate, $[Ru(NH_3)_5]^{3+}$, reaches a maximum value at about 10 seconds after the initiation of reaction, and then decreases slowly, so the steady-state approximation can be applicable. The activation parameters for the anation reaction are shown in Table 1.

For the aquation reaction, the rate constant of each elementary process could not be individually determined because the slope and the intercept of the straight line in Fig.1 gave only the values of $k_5' k_7/(k_6+k_7)$ and $k_6k_8/(k_6+k_7)$. The rate constants in the aquation reaction;

$$[RuX(NH_3)_5]^{2+} + H_2O \underset{k_b}{\overset{k_f}{\rightleftharpoons}} [Ru(OH_2)(NH_3)_5]^{3+} + X^- \qquad (9)$$

can be expressed as follows; $k_f = k_5'k_7/(k_6+k_7)$, $k_b = k_6k_8/(k_6+k_7)$. The values of k_f and k_b are controlled by the rate constants k_5' and k_8 in the respective rate-determining-step. The values of k_f, k_b and the activation parameters for them were given in Table 1. The activation energies for k_1 and k_4 are larger than those for k_f and k_b. This fact also supports that the aquation reaction takes the S_N 2 mechanism, while the anation reaction proceeds through the S_N 1 mechanism.

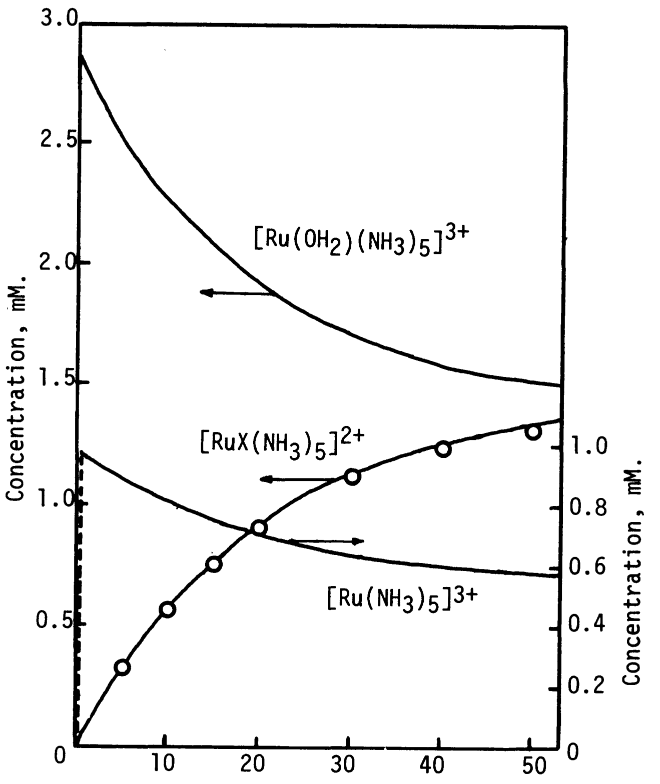

Fig.3. Time-conversion curves for the anation reaction ($([Ru(OH_2)(NH_3)_5]^{3+})_{t=0}$ =0.285 mM; $[X^-]$=10 mM; pH=2.0; μ=1.00. -o- Experimental,—— Simulation.

The calculations were performed on FACOM-230-25 Computer at the Engineering Search Center of Kumamoto University.

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