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NON-STEADY STATE STUDY ON THE BASE HYDROLYSIS OF MONOIODOPENTAAMMINERUTHENIUM(III) COMPLEX

Hiroyuki SAKAMOTO, Haruo MAKINO, Keijiro HAMADA, and Akira OHYOSHI
Department of Industrial Chemistry, Faculty of Engineering,
Kumamoto University, Kumamoto Kurokami 860

A new mechanism on the base hydrolysis of monoiodopentaammineruthenium(III) complex has been proposed by means of analysis of the non-steady state reaction. The reaction is well accounted by a mechanism involving S_N2 CB and S_N2 processes:

$$[RuI(NH_3)_5]^{2+} + OH^- \rightleftharpoons [RuI(NH_3)_4(NH_2)]^+ + H_2O$$

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

$$[RuI(NH_3)_5]^{2+} + OH^- \longrightarrow [Ru(OH)(NH_3)_5]^{2+} + I^-$$

The base hydrolysis of monohalogenopentaammineruthenium(III) complexes has been studied[1,2]. However, no paper mentions the non-steady state period of the initial reaction stage. This paper deals with the initial stage of the reaction and propose a new mechanism.

The monoiodopentaammineruthenium(III) complex was prepared by the method of literature[3]. The ionic strength of the reaction solutions were adjusted to 1.0 mol·kg^{-1}, and the concentration of hydroxide-ion to 3.0×10^{-2}M ∿ 2.0×10^{-1} M (M=mol·dm^{-3}) with sodium hydroxide and sodium perchlorate. All the reaction temperatures were kept to (15.0 ± 0.1)°C. The reaction rate was followed by the decrease in the absorbance at 545 nm, a Hitachi 124 recording spectrophotometer being used.

As is shown in Fig.1, some deviations from the straight lines of the first-order plots are observed in the initial period of the reaction, that is, the reaction has not yet been reached at the steady state. This fact suggests that the measured absorbance involves simultaneously not only that of the reactant but also that of an intermediate. If the intermediate is the amido-complex, which is the conjugated base of reactant, it may be acceptable that the values of λ_{max} and extinction coefficient of the intermediate are nearly equal to those of the reactant.

In this reaction, we assumed the following mechanism :

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

$$[RuI(NH_3)_4(NH_2)]^+ + OH^- \xrightarrow{k_2,\ H_2O} [Ru(OH)(NH_3)_5]^{2+} + I^- + OH^- \quad (2)$$

$$[RuI(NH_3)_5]^{2+} + OH^- \xrightarrow{k_3} [Ru(OH)(NH_3)_5]^{2+} + I^-. \quad (3)$$

The complete rate equations are given by

$$d[A]/dt = -(k'_1+k'_3)[A] + k'_{-1}[B]. \quad (4)$$

$$d[B]/dt = k_1'[A] - (k_{-1}'+k_2')[B], \qquad (5)$$

$$d[C]/dt = k_2'[B] + k_3'[A]. \qquad (6)$$

The rate of transformation of reactant A and intermediate B can be obtained from Eqs.4 and 5.

$$d([A]+[B])/dt = k_2'[B] - k_3'[A] \qquad (7)$$

Introducing the initial conditions to the solutions of Eqs.4 ∿ 7, we obtain

$$[A] = \{(k_1'+k_3'-\lambda_2)e^{-\lambda_1 t} - (k_1'+k_3'-\lambda_1)e^{-\lambda_2 t}\}[A]_0/(\lambda_1-\lambda_2) \qquad (8)$$

$$[B] = (-e^{-\lambda_1 t} + e^{-\lambda_2 t})k_1'[A]_0/(\lambda_1-\lambda_2) \qquad (9)$$

$$[C] = \{(\lambda_2-k_3')e^{-\lambda_1 t} - (\lambda_1-k_3')e^{-\lambda_2 t}\}[A]_0/(\lambda_1-\lambda_2) + [A]_0 \qquad (10)$$

$$[A]+[B] = \{(k_3'-\lambda_2)e^{-\lambda_1 t} - (k_3'-\lambda_1)e^{-\lambda_2 t}\}[A]_0/(\lambda_1-\lambda_2). \qquad (11)$$

where $A=[RuI(NH_3)_5]^{2+}$, $B=[RuI(NH_3)_4(NH_2)]^+$, $C=[Ru(OH)(NH_3)_5]^{2+}$, $\lambda_1=(p+\sqrt{p^2-4q})/2$, $\lambda_2=(p-\sqrt{p^2-4q})/2$, $p=k_1'+k_{-1}'+k_2'+k_3'$, $q=k_1'k_2'+k_{-1}'k_3'+k_2'k_3'$, $k_1'=k_1[OH^-]$, $k_{-1}'=k_{-1}[H_2O]$, $k_2'=k_2[OH^-]$, $k_3'=k_3[OH^-]$. Subscript zero indicates the initial concentration.

The Equation 11 is described by

$$[A]+[B] = C_1e^{-\lambda_1 t} + C_2e^{-\lambda_2 t} \qquad (11')$$

where C_1 and C_2 are constants.

In the steady state period, the first term of right-hand of Eq.11' is nearly equal to zero. So we can obtain λ_2 value by plots of $\ln\{([A]+[B])/\mathrm{mol\cdot dm^{-3}}\}$ vs. time. The λ_1 value is evaluated by plots of $\ln\{(C_2e^{-\lambda_2 t}-([A]+[B])/\mathrm{mol\cdot dm^{-3}}\}$ vs. time. The λ_2 and λ_1 correspond to respective slopes of the straight line in Figs.1. and 2. Plots of $\lambda_1+\lambda_2(=p)$ and $\lambda_1\cdot\lambda_2(=q)$ vs. concentration of hydroxide ion are shown in Fig.3. The slope and intercept of the straight line indicate $k_1+k_2+k_3$ and k_{-1} values respec-

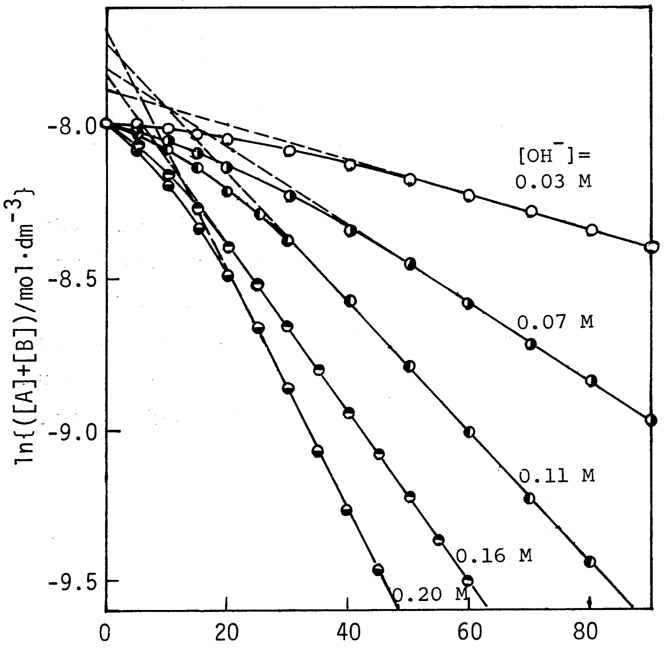

Fig.1. Plots of ln([A]+[B]) vs. reaction time. A: $[RuI(NH_3)_5]^{2+}$, B: $[RuI(NH_3)_4(NH_2)]^+$.

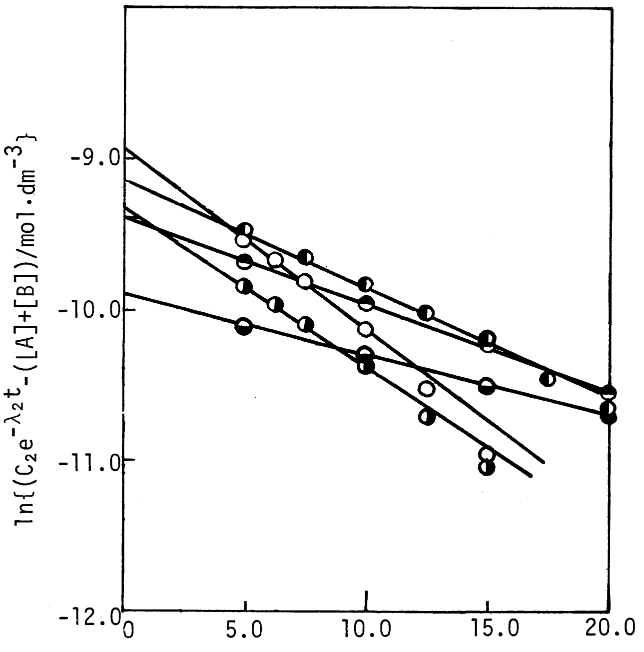

Fig.2. Plots of $\ln\{C_2e^{-\lambda_2 t}-([A]+[B])/\mathrm{mol\cdot dm^{-3}}\}$ vs. reaction time. A: $[RuI(NH_3)_5]^{2+}$ B: $[RuI(NH_3)_4(NH_2)]^+$ $[OH^-]$; -◒- 0.03 M, -⊖- 0.07 M, -◐- 0.11 M, -◑- 0.16 M, -○- 0.20 M.

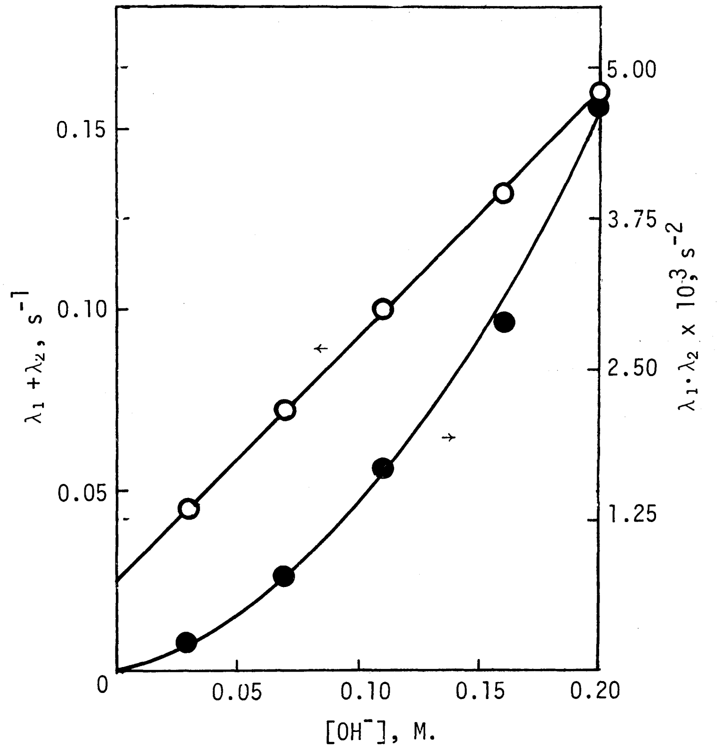

Fig.3. Plots of $\lambda_1+\lambda_2$ and $\lambda_1\cdot\lambda_2$ vs. [OH^-].

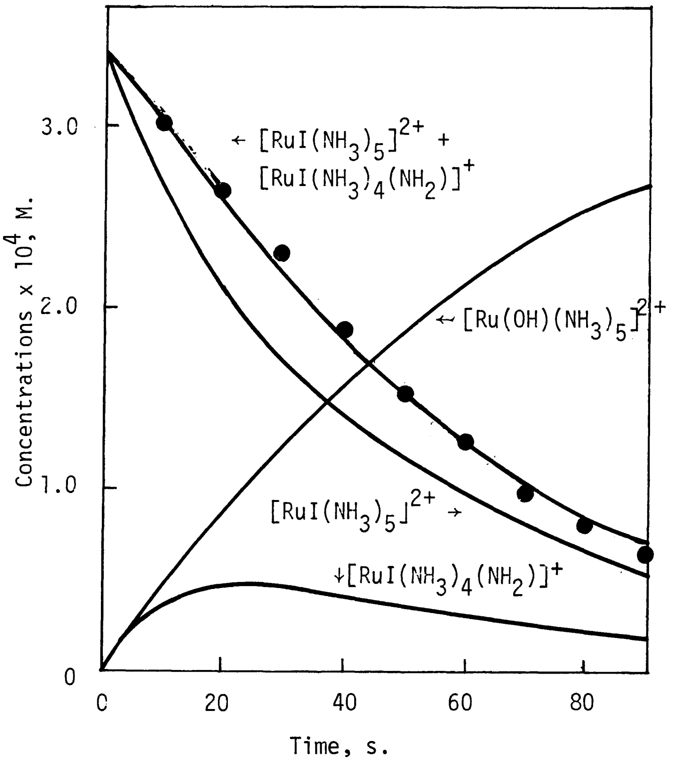

Fig.4. Simulation analysis of time-conversion curves. $[RuI(NH_3)_5]^{2+}_0$ =3.42 x 10^{-4} M, [OH^-] = 0.11 M, Temp = 15.0°C, μ = 1.0 mol·kg^{-1}, k_1, k_2, k_3 and k_{-1} are 1.57 x 10^{-1} $M^{-1}s^{-1}$, 4.15 x 10^{-1} $M^{-1}s^{-1}$, 9.31 x 10^{-2} $M^{-1}s^{-1}$, and 2.70 x 10^{-2} s^{-1} respectively. ●, Experimental; ——, Simulation.

tively. The k_3 value was estimated from the slope of the tangent of the time-conversion curve at the reaction time, t=0 (Fig.4). The values of k_1 and k_2 were calculated from the relationship between p and q. Thus, all the rate constants are available to be $k_1 = 1.57\text{x}10^{-1}M^{-1}s^{-1}$, $k_{-1} = 2.70\text{x}10^{-2}$ s^{-1}, $k_2 = 4.15\text{x}10^{-1}M^{-1}s^{-1}$, and $k_3 = 9.31\text{x}10^{-2}M^{-1}s^{-1}$ respectively. It seems that the dissociation of hydrogen is very difficult in comparison with the hydrogen exchange reaction of hexaammineruthenium(III) complex[4].

Finally, we carried out the simulation analysis based on the Eqs.(8-11) to check the validity of the estimated rate constants. The result is shown in Fig.4. The time-conversion curve for the total concentration of the reactant and the intermediate obtained from the simulation is in agreement with the experimental values.

Concerning the influence of hydrogen peroxide on the reaction rate of the base hydrolysis of metal ammine complexes, it has been known that the rate constant for the base hydrolysis taking the S_N1 CB mechanism decreases on the addition of hydrogen peroxide, while it increases for the reaction involving the S_N2 process[5].

In the present experiment, it was found that the rate constant obtained in the solution of 0.11 M hydroxide-ion and 0.11 M hydrogen peroxide was about three times that in the solution of 0.11 M hydroxide-ion concentration. From the result, it may be concluded that the S_N2 mechanism is suitable for the present base hydrolysis reaction.

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

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