Simulation Analysis of the Acid-catalyzed Hydrolysis of Carboxylatopentammineruthenium(III) Complexes

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The mechanism of the acid-catalyzed hydrolysis of $(NH_3)_5RuO_2CR^{2+}$ (R=H, CH_3, C_2H_5, $(CH_3)_2CH$, CH_2OH, and/or CH_2NH_2) has been established by the trapezoidal simulation analyses with a computer. The proposed reaction sequences of S_N1 combined with S_N2 mechanisms involving a quasi-stable intermediate $(NH_3)_5Ru^{3+}$ have proved to be plausible, and the kinetic parameters (rate constants, $\Delta H^{\neq}$, $\Delta S^{\neq}$, *etc.*) have been given for all of the elementary reactions. The aquation rate has been determined by the solvent-assisted, heterolytic dissociation of $(NH_3)_5RuO_2CR^{2+}$ and follows this order: formato>acetato>propionato>isobutyrato>glycolato>glycinato.

In the previous paper,[1] the acid hydrolyses of alkyl-, hydroxyl-, and/or amino-substituted-carboxylatopentaammineruthenium(III) complexes ($(NH_3)_5RuO_2CR^{2+}$) have been proved to proceed in the pseudo first-order fashion:

$$(NH_3)_5RuO_2CR^{2+} + H_2O \xrightarrow[k_{obs}]{H^+} (NH_3)_5RuOH_2^{3+} + RCO_2^- \quad (1)$$

The pseudo first-order rate constant, k_{obsd}, can be represented by the acid-dependent and acid-independent rate constants, k_H and k_d respectively, with a good analytic fit:[1]

$$k_{obs} = k_H[H^+] + k_d \quad (2)$$

The kinetic relationship of Eq. (2) has also been established in the aquation of pentaammine-amino acid cobalt(III) complexes.[2,3] The mechanism of such an aquation reaction has been interpreted, in terms of the reaction paths involving the protonated complex, as:

$$(NH_3)_5MOC(=O)R^{n+} + H^+ \overset{K}{\rightleftharpoons} (NH_3)_5MOC(-OH)R^{(n+1)+} \quad (3)$$

$$(NH_3)_5MOC(-OH)R^{(n+1)+} + H_2O \xrightarrow{k} (NH_3)_5MOH_2^{(n+1)+} + RCO_2^- + H^+ \quad (4)$$

where M denotes the central transition metal.

The aquation mechanism, however, has not yet been strictly established, since Reactions (3) and (4) cannot well explain the kinetic expression of Eq. (2).[4]

The present study was undertaken in order to elucidate the mechanism of the acid-catalyzed hydrolysis of $(NH_3)_5RuO_2CR^{2+}$ (R=H, CH_3, C_2H_5, $(CH_3)_2CH$, CH_2OH, and/or CH_2NH_2) using the technique of computer simulation.

Simulation Results and Discussion

Elementary Reactions of Aquation. In view of the kinetic relationship expressed by Eq. (2), Reaction (1) may be considered to consist of the following two reaction paths involving a quasi-stable intermediate of $(NH_3)_5Ru^{3+}$ (*i.e.*, acid-catalyzed S_N2 and acid-independent S_N1 reactions):

$$(NH_3)_5RuO_2CR^{2+} \xrightarrow[k_H]{H^+} (NH_3)_5Ru^{3+} + RCO_2^- \quad (5)$$

$$(NH_3)_5RuO_2CR^{2+} \xrightarrow{k_d} (NH_3)_5Ru^{3+} + RCO_2^- \quad (6)$$

$$(NH_3)_5Ru^{3+} + H_2O \underset{k_e}{\overset{k_{H_2O}}{\rightleftharpoons}} (NH_3)_5RuOH_2^{3+} \quad (7)$$

The corresponding differential terms (rate equations) derived from Eqs. (5)—(7) are:

$$d[(NH_3)_5RuO_2CR^{2+}]/dt = -d[RCO_2^-]/dt = -(k_H[H^+]+k_d)[(NH_3)_5RuO_2CR^{2+}] \quad (8)$$

$$d[(NH_3)_5Ru^{3+}]/dt = (k_H[H^+]+k_d)[(NH_3)_5RuO_2CR^{2+}] + k_e[(NH_3)_5RuOH_2^{3+}] - k'_{H_2O}[(NH_3)_5Ru^{3+}] \quad (9)$$

$$d[(NH_3)_5RuOH_2^{3+}]/dt = k'_{H_2O}[(NH_3)_5Ru^{3+}] - k_e[(NH_3)_5RuOH_2^{3+}] \quad (10)$$

where k_{H_2O}' stands for the pseudo first-order rate constant derived from $k_{H_2O}[H_2O]$. Assuming the stationary-state for the concentration of $(NH_3)_5Ru^{3+}$, Eq. (2) can be reproduced as:

$$-d[(NH_3)_5RuO_2CR^{2+}]/dt = d[(NH_3)_5RuOH_2^{3+}]/dt = \{k_H[H^+]+k_d\}[(NH_3)_5RuO_2CR^{3+}] \quad (11)$$

Some remarks on Reactions (5) and (6) should be made here in connection with the molecular interaction between $(NH_3)_5RuO_2CR^{2+}$ and H^+ and/or the H_2O solvent. From the results of the extended Hückel MO calculations of the above interacting systems, the most plausible interactions of H^+ and H_2O with $(NH_3)_5RuO_2CR^{2+}$ occur, respectively, in the direction of the orbital expansion of the nonbonding lone-pair 2p-orbital on the oxygen atom of the Ru–O bond and in that of the lowest-unoccupied, antibonding dp-σ orbital on the Ru–O bond axis, which leads to a weakening of the Ru–O.[5] The acid-catalyzed and the solvent-assisted dissociation processes (reactions (5) and (6) respectively) are energetically comparable with the heterolytic cleavage of the Ru–O (see the $\Delta H^{\neq}$ values in Table 2). It is worthy of emphasis that the constants

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

2) K. Ogino, T. Murakami, and K. Saito, *ibid.*, **41**, 1615 (1968).

3) T. Murakami, K. Ogino, H. Kobayashi, H. Yamasaki, and K. Saito, *ibid.*, **44**, 120 (1971).

4) The present extensive study corrects and unveils some discrepancies in the aquation mechanism proposed previously in Ref. 1.

5) The discussions referred to in the remarks made above will be developed in detail in a succeeding paper.

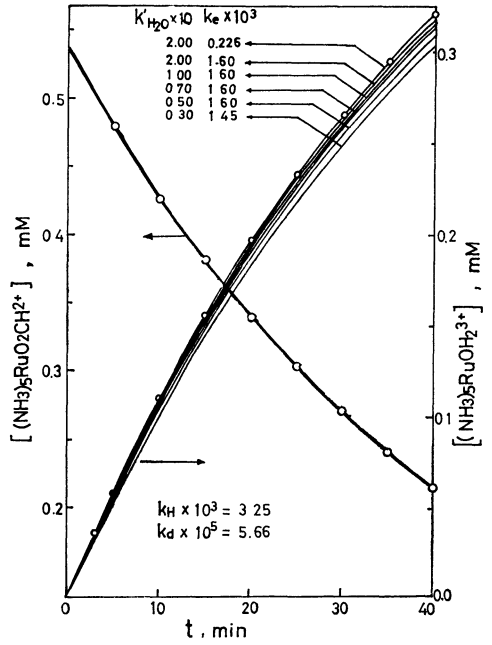

Fig. 1. Variations in time conversions of $[(NH_3)_5RuO_2CH^{2+}]$ and $[(NH_3)_5RuOH_2^{3+}]$ with various sets of values of k_H, k_d, k'_{H_2O}, and k_e at 61°C: $[(NH_3)_5RuO_2CH^{2+}]_i=0.536$ mM; $[H^+]=0.1$ M; $\mu=0.1$.
——: Simulation, ○: Experiment

of k_H and k_d seem to be pseudo rate constants, *i.e.*, $k_H'[H_2O]$ and $k_d'[H_2O]$ respectively.

Determination of the Rate Constants. We will determine the rate constants of the elementary reactions expressed by Eqs. (5)—(7) on the basis of the simulation analysis. Figure 1 indicates the dependence of the time conversions of $[(NH_3)_5RuO_2CR^{2+}]$ and $[(NH_3)_5RuOH_2^{3+}]$ upon various values of k_H, k_d, $k_{H,O}'$, and k_e for the formato-complex. The values of k_H and k_d obtained experimentally[1] for the formato-complex show a good analytic fit, while the best values of $k_{H,O}'$ and k_e were found to be 2.00×10^{-1} M^{-1} s^{-1} and 2.26×10^{-4} s^{-1} respectively; the latter k_e value was obtained from the anation studies[6] of $(NH_3)_5RuOH_2^{3+}$ under the same reaction conditions. The validity of the above values of $k_{H,O}'$, k_e, k_H, and k_d will be tested in the acid hydrolysis of $(NH_3)_5RuO_2CR^{2+}$, where R denotes an alkyl group. As can be seen from Fig. 2, the simulated time conversions of $[(NH_3)_5RuO_2CR^{2+}]$ and $[(NH_3)_5RuOH_2^{3+}]$ are in satisfactory accordance with the experimental values. Table 1 shows the values of k_{obsd}, k_H, k_d, $k_{H,O}'$, and k_e in the Arrhenius-type equations, which were determined by a further simulation analysis of the complex-hydrolyses in the acid solution ($[H^+]=0.025$—0.1 M) at the temperatures of 40, 50, and 70 °C under the condition of $\mu=0.1$. As may be seen from Table 1, the relationship shown by Eq. (2) is completely accounted for.[7]

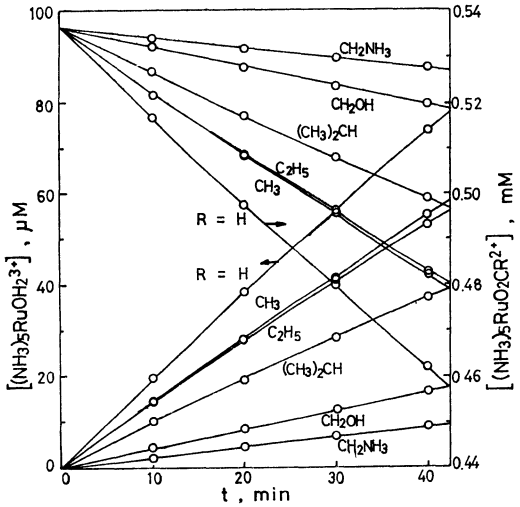

Fig. 2. Simulated time-conversions of $[(NH_3)_5RuO_2CR^{2+}]$ and $[(NH_3)_5RuOH_2^{3+}]$ *vs.* experimental ones: $[(NH_3)_5RuO_2CR^{2+}]_i=0.536$ mM; $[H^+]=0.1$ M; $\mu=0.1$; $T=40$ °C.
——: Simulation, ○: Experiment

Reaction Sequences. Now, let us discuss the validity of the reaction schemes represented by Eqs. (5)—(7). From the rate equations of Eqs. (8)—(10), the time-dependence of the [reactant], the [intermediate], and/or the [product] can be reproduced by the non-steady-state analysis:

$$[(NH_3)_5RuO_2CR^{2+}] = [(NH_3)_5RuO_2CR^{2+}]_i e^{-\lambda_1 t} \quad (12)$$

$$[(NH_3)_5Ru^{3+}] = [(NH_3)_5RuO_2CR^{2+}]_i[(1-e^{-\lambda_1 t}) - k'_{H,O}(e^{-\lambda_1 t}-e^{-\lambda_1 t})/(\lambda_2-\lambda_1) - (e^{-\lambda_1 t}-1)/\lambda_2] \quad (13)$$

$$[(NH_3)_5RuOH_2^{3+}] = k'_{H,O}[(NH_3)_5RuO_2CR^{2+}]_i \times [(e^{\lambda_1}-e^{\lambda_1})/(\lambda_2-\lambda_1) - (e^{\lambda_1}-1)/\lambda_2] \quad (14)$$

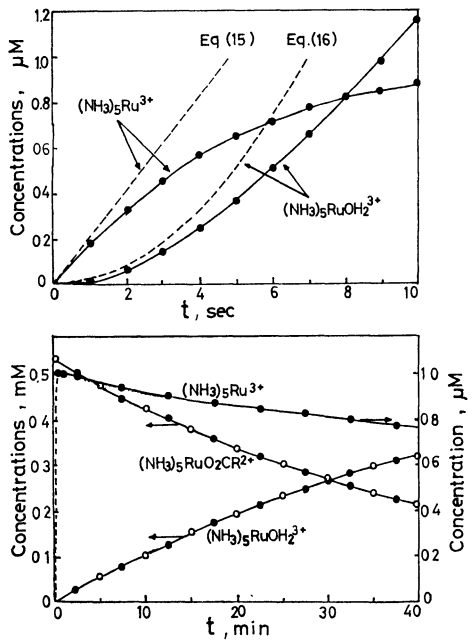

Fig. 3. Time conversions of $[(NH_3)_5RuO_2CR^{2+}]$, $[(NH_3)_5Ru^{3+}]$, and $[(NH_3)_5RuOH_2^{3+}]$ for formato-complex. (Reaction conditions were the same ones in Fig. 1.)
○: from experiments; ●: from Eqs. (12)—(14); —: from simulations

6) A. Ohyoshi, S. Shida, S. Izuchi, F. Kitagawa, and K. Ohkubo, This Bulletin, **46**, 2431 (1973).

7) Strictly speaking, Eq. (2) can be adopted at $t\gtrsim20$ s (see Fig. 3). At $t\gtrsim20$ s, the stationary-state treatment for [intermediate] is possible. In Table 1, the relative errors of the sum of $k_H[H^+]$ and k_d values against k_{obsd} ones (*viz.* $(k_{obsd}-(k_H[H^+]k_d))/k_{obsd}\times100\%$) fall in the range of 0.06—1.15% except in the cases of the propionate- and glycinate-complexes (below 4.60 and 7.45% respectively).

Table 1. The rate constants for the acid-catalyzed hydrolyses of $(NH_3)_5RuO_2CR^{2+}$

$(NH_3)_5RuO_2CR^{2+}$ (R)	Over-all reaction k_{obsd} s^{-1}	Reaction (5) k_H $M^{-1}s^{-1}$	Reaction (6) k_d s^{-1}
H	$5.757\times10^{8}e^{-18580/RT}$	$2.493\times10^{9}e^{-18130/RT}$	$2.277\times10^{10}e^{-21820/RT}$
CH_3	$2.198\times10^{10}e^{-21060/RT}$	$1.361\times10^{10}e^{-18700/RT}$	$2.000\times10^{10}e^{-24790/RT}$
C_2H_5	$8.061\times10^{10}e^{-21800/RT}$	$5.016\times10^{9}e^{-19490/RT}$	$9.723\times10^{15}e^{-30290/RT}$
$(CH_3)_2CH$	$1.547\times10^{11}e^{-22440/RT}$	$2.643\times10^{10}e^{-20180/RT}$	$5.127\times10^{12}e^{-25360/RT}$
CH_2OH	$1.154\times10^{11}e^{-22850/RT}$	$2.491\times10^{11}e^{-22220/RT}$	$1.797\times10^{11}e^{-23940/RT}$
CH_2NH_2	$3.823\times10^{12}e^{-25430/RT}$	$4.970\times10^{17}e^{-33290/RT}$	$1.919\times10^{12}e^{-25020/RT}$

For Reaction (7), $k'_{H_2O}=4.678e^{-2094/RT}$ and $k_e=6.999e^{-6869/RT}$ s^{-1}.

Table 2. The kinetic parameters of activation for the acid-catalyzed hydrolyses of $(NH_3)_5RuO_2CR^{2+}$

$(NH_3)_5RuO_2CR^{2+}$ (R)	Over-all reaction		Reaction (5)		Reaction (6)	
	ΔH^* (kcal/mol)	$-\Delta S^*$ (eu)	ΔH^* (kcal/mol)	$-\Delta S^*$ (eu)	ΔH^* (kcal/mol)	$-\Delta S$ (eu)
H	17.92±0.12	20.67±0.35	17.48±0.02	17.73±0.05	20.18±0.92	14.86±2.79
CH_3	20.42±0.05	13.40±0.15	18.05±0.29	14.37±0.11	24.14±0.05	4.43±0.14
C_2H_5	21.15±0.20	10.91±0.61	18.84±0.04	16.53±0.89	29.64±0.14	12.40±0.44
$(CH_3)_2CH$	21.84±0.19	9.61±0.58	19.52±0.29	13.23±0.87	24.70±0.01	2.57±0.02
CH_2OH	22.20±0.05	10.14±0.14	21.56±0.31	8.81±0.92	23.33±0.44	9.66±1.32
CH_2NH_2	24.75±0.12	3.23±0.37	32.62±0.82	−18.9±2.58	24.34±0.05	4.58±0.15

For Reaction (7), Forward: $\Delta H^*=1.44\pm0.05$kcal/mol; $-\Delta S^*=57.67\pm0.02$ e.u.
Backward: $\Delta H^*=6.22\pm0.00$ kcal/mol; $-\Delta S^*=56.87\pm0.01$ e.u.

where $\lambda_1=k_H[H^+]+k_d$, $\lambda_2=k_{H_2O}'+k_e$, and the subscript i=initial state. As Fig. 3 indicates, the time conversions of the [component] calculated from Eqs. (12)—(14) are in complete agreement with those obtained from the experimental and simulation results. It may be deduced, therefore, that the acid-catalyzed hydrolysis of $(NH_3)_2RuO_2CR^{2+}$ proceeds *via* the reaction sequences proposed (Eqs. (5)—(7)).

Remark should be here made on the concentration-change of components produced during the initial short stage of the reaction. From Eqs. (13)—(14), the [component] values may be approximated as:

$$[(NH_3)_5Ru^{3+}] \approx k'_{H_2O}[(NH_3)_5RuO_2CR^{2+}]_i\times\lambda_1 t \quad (15)$$

$$[(NH_3)_5RuOH_2^{3+}] \approx k'_{H_2O}[(NH_3)_5RuO_2CR^{2+}]_i\times\lambda_1 t^2/2 \quad (16)$$

As can be seen from Fig. 3, Eqs. (15) and (16) reproduce the reaction for at least 1.0 s after the start of the reaction. Moreover, the initial rates of the formation or consumption of the components, r_i[C], can be represented by extended analysis[8] in the case of a formato-complex:

$$r_i[(NH_3)_5RuO_2CR^{2+}] \approx -1.53\times10^{-3}[(NH_3)_5RuO_2CR^{2+}]_i^{0.975}[H^+]_i^{0.699} \text{ M/s}$$

$$r_i[(NH_3)_5Ru^{3+}] \approx 3.12\times10^{-4}[(NH_3)_5RuO_2CR^{2+}]_i^{1.000}[H^+]_i^{0.702} \text{ M/s}$$

$$r_i[(NH_3)_5RuOH_2^{3+}] \approx 1.57\times10^{-3}[(NH_3)_5RuO_2CR^{2+}]_i^{1.000}[H^+]_i^{0.704} \text{ M/s}$$

Kinetic Parameters of Activation for Elementary Reactions. Mention should be made here of the enthalpy and entropy of activation, ΔH^* and ΔS^*, for each elementary reaction. Using the rate constants listed in Table 1, the least-squares calculations of ΔH^* and ΔS^* values were performed by means of a computer. Table 2 shows the ΔH^* and ΔS^* values for all the elementary reactions. Judging from the ΔH^* values in Table 2, the reaction step of Eq. (6) may be said to determine the over-all reaction rate, except in the case of the glycinato-complex; the reaction rates follow this order: formato>acetato>propionato>isobutyrato>glycolato>glycinato.

Procedure of Simulation

The procedure of non-steady-state simulation will now be interpreted briefly. According to the trapezoidal simulation method,[9] the series of increments ($D(i)$, i=1—4) may be defined by the following terms on the basis of Eqs. (5)—(7):

$$D(1) = k_H[H^+][(NH_3)_5RuO_2CR^{2+}]dt$$

$$D(2) = k_d[(NH_3)_5RuO_2CR^{2+}]dt$$

$$D(3) = k_{H_2O}[H_2O][(NH_3)_5Ru^{3+}]dt = k'_{H_2O}[(NH_3)_5Ru_2^{3+}]dt$$

$$D(4) = k_e[(NH_3)_5RuOH_2^{3+}]dt$$

According to the rate equations of Eqs. (8)—(10), we obtain:

$$D[(NH_3)_5RuO_2CR^{2+}]_{av} = -D(1)_{av} - D(2)_{av}$$

$$D[RCO_2^-]_{av} = D(1)_{av} + D(2)_{av}$$

$$D[(NH_3)_5Ru^{3+}]_{av} = D(1)_{av} + D(2)_{av} - D(3)_{av} + D(4)_{av}$$

$$D[(NH_3)_5RuOH_2^{3+}]_{av} = D(3)_{av} - D(4)_{av}$$

where the average increments, D_{av}, are evaluated from $(D_t+D_{t+dt})/2$, by the use of the increments at the reaction times of t and $t+dt$, as D_t and D_{t+dt} respec-

8) The analytical method was similar to that described in detail in Ref. 9.

9) K. Ohkubo and T. Hashimoto, This Bulletin, **45**, 3350 (1972).

tively.

The desired concentrations of the components, C (reactant, intermediate, and product), $[C]_t$, at the reaction time, t, can be calculated by:

$$[C]_t = [C]_i + \sum^{n} D[C]_{av} \qquad (ndt = t)$$

where $[C]_i$ and $D[C]_{av}$ are, respectively, the initial concentration of the component, C, and the over-all increment (or decrement) changing with t. In this paper, the $[C]_t$ values were evaluated every 0.1 s (in the case of the initial short stage of the reaction, dt=0.02 s).