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ESTIMATING MECHANISM AND KINETIC RATE CONSTANTS USING ITERATIVE SEARCH TECHNIQUE I, ANATION REACTION OF AQUOPENTAAMMINERUTHENIUM(III) COMPLEXES IN AQUEOUS SOLUTION

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The elementary reaction mechanism and the kinetic rate constants for the anation reaction of aquopentaammineruthenium(III) complexes are estimated by a new iterative search technique. The anation mechanism is well illustrated by the S_N1 and S_N2 combined reaction map. The five-coordinated species participates directly in the reaction as a momentarily living intermediate, and the seven-coordinated species seems to be allowed only in the transition state.

Recent kinetic interest has centered around the elucidation of momentarily living intermediates participating in the reaction system. The usual kinetic treatment of the mechanism, however, hardly brings about a precise reaction map illustrating the elementary reaction steps, because it often meets with a difficulty in estimating all the rate constants of the steps.

In the present paper, a new iterative search technique will be shown to be useful for estimating kinetic rate constants, taking a kinetic example of the following anation reaction:

$$ML_5H_2O^{3+} + X^- \rightleftharpoons ML_5X^{2+} + H_2O \qquad (1)$$

where $ML_5H_2O^{3+}$=aquopentaammineruthenium(III) complex; X^-=monohalogenoacetate ion; ML_5X^{2+}=monohalogenoacetatopentaammineruthenium(III) complex.

In illustrating and developing the technique, we will discuss three representative anation mechanisms, Mechanisms I, II, and III, and determine the best mechanism:

Mechanism I (limiting S_N1 reaction[1-4])

$ML_5H_2O^{3+} \xrightleftharpoons[k_2]{k_1} ML_5^{3+} + H_2O$ (2a) $ML_5^{3+} + X^- \xrightleftharpoons[k_4]{k_3} ML_5X^{2+}$ (2b)

Mechanism II (S_N1 and S_N2 combined reaction)

$ML_5H_2O^{3+} \xrightleftharpoons[k_2]{k_1} ML_5^{3+} + H_2O$ (3a) $ML_5^{3+} + X^- \xrightleftharpoons[k_4]{k_3} ML_5X^{2+}$ (3b)

$ML_5H_2O^{3+} + X^- \xrightleftharpoons[k_6]{k_5} ML_5X^{2+} + H_2O$ (3c)

Mechanism III (nucleophile-annexed reaction)

$ML_5H_2O^{3+} + X^- \xrightleftharpoons[k_2]{k_1} ML_5H_2O\text{--}X^{2+}$ (4a) $ML_5H_2O\text{--}X^{2+} \xrightleftharpoons[k_4]{k_3} ML_5X^{2+} + H_2O$ (4b)

Mechanisms I, II, and III are characterized respectively by a five-coordinated intermediate, a five-coordinated intermediate and a seven-coordinated species in the transition state, and a seven-coordinated intermediate.

Computation Method

The nonstationary-state solution of the differential equations derived from Eqs.(2a-b), (3a-c), or (4a-b) gives the concentration of ML_5X^{2+} at t, $(ML_5X^{2+})_{t,calcd}$, as:

$$(ML_5X^{2+})_{t,calcd}=k_1k_3(X^-)(ML_5H_2O^{3+})_0[(\gamma_2e^{-\gamma_1t}-\gamma_1e^{-\gamma_2t})/(\gamma_1-\gamma_2)+1]/a \quad \text{----- (Mechanism I)} \qquad (5)$$

$$(ML_5X^{2+})_{t,calcd}=(ML_5H_2O^{3+})_0[((q\delta_2-k_5(X^-)p)e^{-\delta_1t}-(q\delta_1-k_5(X^-)p)e^{-\delta_2t})/(\delta_1-\delta_2)+q]/p \quad \text{----- (Mechanism II)} \qquad (6)$$

$$(ML_5X^{2+})_{t,calcd}=k_1k_3(X^-)(ML_5H_2O^{3+})_0[(\lambda_2e^{-\lambda_1t}-\lambda_1e^{-\lambda_2t})/(\lambda_1-\lambda_2)+1]/u \quad \text{----- (Mechanism III)} \qquad (7)$$

where $a=k_1k_3(X^-)+k_1k_4+k_2'k_4$; $p=k_1k_3(X^-)+k_1k_4+k_1k_6'+k_2'k_4+k_2'k_5(X^-)+k_2'k_6'+k_3k_5(X^-)^2+k_3k_6'(X^-)+k_4k_5(X^-)$; $q=k_1k_3(X^-)+k_3k_5(X^-)^2+k_2'k_5(X^-)$; $u=k_1k_3(X^-)+k_1k_4'(X^-)+k_2k_4'$; $\gamma_1=b+\sqrt{b^2-4a}$; $\gamma_2=b-\sqrt{b^2-4a}$; $\delta_1=r+\sqrt{r^2-4p}$; $\delta_2=r-\sqrt{r^2-4p}$; $\lambda_1=v+\sqrt{v^2-4u}$; $\lambda_2=v-\sqrt{v^2-4u}$; $b=k_1+k_2'+k_3(X^-)+k_4$; $r=k_1+k_2'+k_3(X^-)+k_4+k_5(X^-)$; $v=k_1(X^-)+k_2+k_3+k_4'$; k_2', k_4', and k_6'= pseudo first-order rate constants; the subscript zeros=initial state.

The rate constants, k_i, are supplied from those falling in the range from a lower limit ($\min k_i$) to an upper limit ($\max k_i$):

$$k_i=\min k_i + \sum^{\alpha n}\Delta k_i/\alpha, \quad \Delta k_i=(\max k_i - \min k_i)/\alpha n \qquad (\alpha=10^m,\ m=0,1,2,\text{---}) \qquad (8)$$

where Δk_i=step size for k_i; α=coefficient determining the number of significant figure for k_i.

The parameter estimation procedure is, then, developed by minimizing the relative error computed by Eq.(9), ε_σ (σ=checking point number), changing one of the rate constants, k_j, in turn with the fixed $k_{i(i \neq j)}$ values:

$$\varepsilon_\sigma = \left|(ML_5X^{2+})_{t,calcd} - (ML_5X^{2+})_{t,given}\right| / (ML_5X^{2+})_{t,given} \times 10^2 \qquad (9)$$

where $(ML_5X^{2+})_{t,given}$ stands for the given concentration of ML_5X^{2+} obtained from our laboratory measurements.

Then, the best rate constants are estimated by changing the number of significant figure for k_i under the following error norm:

$$\varepsilon = \sum_\sigma \varepsilon_\sigma < \delta\varepsilon \qquad (10)$$

where $\delta\varepsilon$ denotes a condition for the convergence of computation.

Throughout the present study, $\max k_i = 1.0 \times 10^4$, $\min k_i = 1.0 \times 10^{-9}$, and σ=1, 2, and 3 (t=5, 10, and 20 min respectively) are used for estimating the rate constants of the anation reaction at 60.0°C for 60 min (μ=0.1 - 0.2) over the concentration ranges of $(ML_5H_2O^{3+})_0$=0.536 mM and $(X^-)_0 = 5.0 \times 10^{-3} - 1.0 \times 10^{-1}$ M.

Computation Results and Discussion

Let us first show an example of computation results in the estimates of the rate constants for the anation reaction **represented** by Mechanism I. As Table 1

Table 1. An Example of Computed Results

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          ESTIMATING KINETIC RATE CONSTANTS USING ITERATIVE SEARCH TECHNIQUE

                    ANATION OF PENTAAMMINERUTHNIUM(III) COMPLEX WITH
                MONOCHLOROACETIC ACID AT 60.0 DEG. (IONIC STRENGTH=0.2)

    MECHANISM I     INITIAL SPECIFICATIONS  AQUO-COMPLEX CONC.=0.536MM
                                            MONOCHLOROACETIC ACID CONC.=0.05M
      GIVEN KINETIC DATA    PRODUCT CONC. (M UNIT)
                POINT 1=0.1090E-03   POINT 2=0.1942E-03   POINT 3=0.3128E-03

           RANGE OF SUPPLIED RATE CONSTANTS   MINKI=0.10E-08   MAXKI=0.10E 05


FIRST (OR PSEUDO FIRST) ORDER RATE CONSTANTS        RELATIVE ERRORS (PERCENT)

   K1         K2         K3         K4           POINT 1      POINT 2      POINT 3

 0.9E 00    0.4E-03    0.8E-03    0.1E-03      0.307E 01    0.220E 01    0.521E 00
 0.1E 00    0.5E-03    0.8E-03    0.1E-03      0.321E-01    0.679E 00    0.181E 00
0.10E 00   0.46E-03   0.80E-03   0.97E-04      0.433E-01    0.792E 00    0.997E-02
0.99E-01   0.47E-03   0.80E-03   0.97E-04      0.307E-02    0.746E 00    0.256E-01

                                  ITERATION NUMBER ( 4)

      ** BEST RATE CONSTANTS **             ** SUM OF RELATIVE ERRORS (PERCENT) **

0.99E-01   0.47E-03   0.80E-03   0.97E-04              0.793E 00
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Table 2. Estimates of Anation Rate Constants.[a)]

Mechanism I

X^-	$k_{obsd}x10^4$	k_1x10^2	$k_2^!x10^3$	k_3x10^2	k_4x10^4	ε_1	ε_2	ε_3	ε(%)
$FCH_2CO_2^-$	6.73	3.1	2.4	1.6	1.0	1.727	1.429	0.020	3.18
$ClCH_2CO_2^-$	8.22	9.9	4.7	1.6	1.0	0.003	0.764	0.026	0.793

Mechanism II

X^-	$k_{obsd}x10^4$	k_1x10^4	$k_2^!x10$	k_3x10	k_4x10^5	k_5x10^2	$k_6^!x10^4$	ε_1	ε_2	ε_3	ε(%)
$FCH_2CO_2^-$	6.73	2.3	2.0	4.8	0.035	1.3	0.37	0.032	0.665	0.0	0.697
$ClCH_2CO_2^-$	8.22	2.3	2.0	6.4	2.2	1.5	0.70	0.028	0.630	0.010	0.668
$BrCH_2CO_2^-$	11.8	2.3	2.0	1.2	21	1.8	1.0	1.109	0.016	0.115	1.240
$ICH_2CO_2^-$	1.02	2.3	2.0	7.2	0.011	1.9	0.60	0.009	0.635	0.029	0.678

Mechanism III

X^-	$k_{obsd}x10^4$	k_1	k_2x10^3	k_3x10^4	$k_4^!x10^4$	ε_1	ε_2	ε_3	ε(%)
$FCH_2CO_2^-$	6.73	0.62	2.4	8.0	1.0	1.727	1.429	0.020	3.176
$ClCH_2CO_2^-$	8.22	2.0	4.7	8.0	1.0	0.003	0.764	0.026	0.793

a) Reaction conditions: $(ML_5H_2O^{3+})_0$=0.536 mM; $(X^-)_0$=0.050 M except $(ICH_2CO_2^-)_0$= 0.005 M; Reaction temperature=60.0°C; μ=0.1 except μ=0.2 in $ClCH_2CO_2^-$.

$k_2^!$, $k_4^!$, and $k_6^!$: Pseudo first-order rate constants in s^{-1} unit.

k_i: Second-order rate constants in $M^{-1}s^{-1}$ unit, except the above pseudo ones.

indicates, the four iterations give the best k_i values written by two significant figures with ε=0.793 %.

In Table 2, the best k_i values estimated by the similar treatments are summarized for Mechanisms I, II, and III. It is noticeable that all the rate constants are estimated within ε=3.2 %. It is deduced, therefore, that the best mechanism seems to be hardly estimated only from the ε values in the fixed initial specifications (so-called initial conditions).

Now, let us examine the validity of the estimated k_i values, with the attention given to the time conversion of (ML_5X^{2+}) under two different initial specifications: $(ML_5H_2O^{3+})_0$=0.536 mM; $(X^-)_0$=0.050 M and 0.10 M. Plotting the (ML_5X^{2+}) values calculated by Eqs.(5)-(7) with the estimated rate constants gives the curves presented in Fig. 1. We observe that the curves of (ML_5X^{2+}) for Mechanism II are in satisfactory accordance with the observed data-points. The curves of (ML_5X^{2+}) for Mechanisms I and III, however, differ appreciably from the observations. This tendency can be recognized in the other cases of the anation reactions of aquopentaammineruthenium(III) complexes: For example, in the anation of the aquo-complex with monofluoroacetic acid, Mechanism II has ε=0.032 - 0.11 % at 5 min and ε=0.68 - 0.66 % at 10 min, while Mechanisms I and III have ε=1.73 - 6.60 % at 5 min and ε=0.68 - 6.60 % at 10 min. Therefore, Mechanism II, the S_N1 and S_N2 combined reaction, seems to be the best mechanism; The five-coordinated intermediate participates directly in the reaction, and the seven-coordinated species seems to be forbidden as an intermediate (if possible, it is expected only in the transition state).

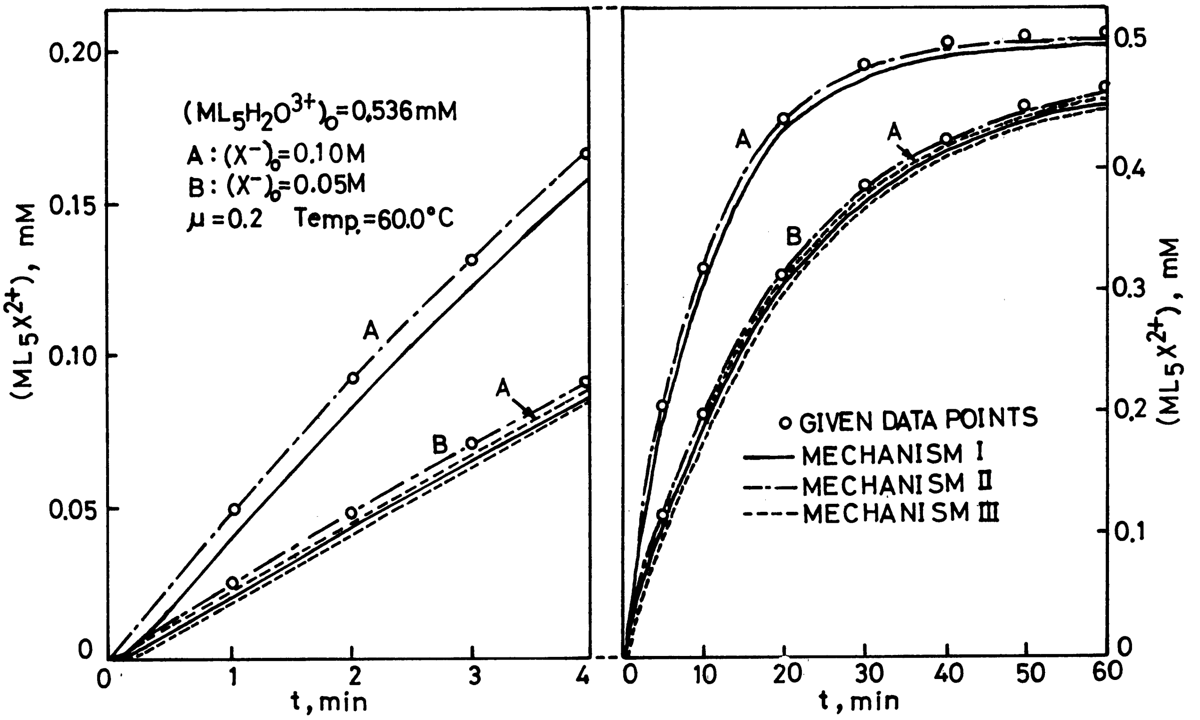

Fig. 1. Time-conversion curves for Mechanisms I, II, and III.

Finally, the evolution of the reaction process in time will be conjectured by the trapezoidal computer simulation[5)] with the estimated rate constants. We will show one example of computed time conversions of the concentrations of the species participating in the anation reaction in Fig. 2.

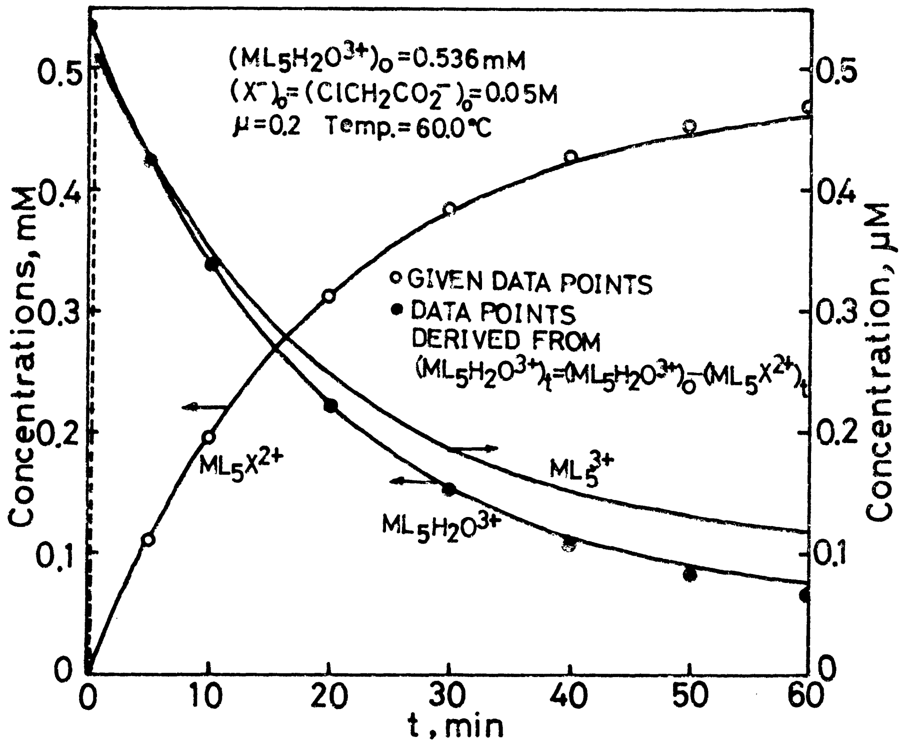

Fig.2. Computer simulation of anation reaction.

The present iterative search technique is, thus, shown to be useful for estimating reaction mechanism and kinetic rate constants.

The calculations were carried out on a FACOM 230-25 computer at the Engineering Search Center of Kumamoto University.

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