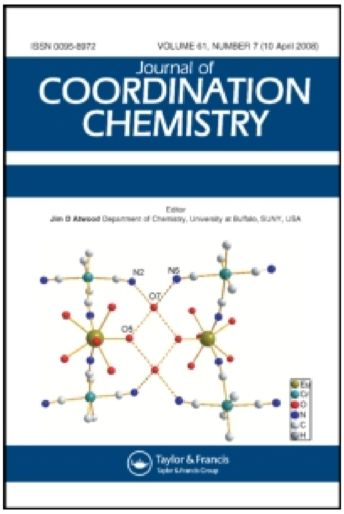

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AQUATION MECHANISM OF MONOHALOGENOACETATOPENTAAMMINE-RUTHENIUM(III) COMPLEXES IN ACID SOLUTIONS

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Key Words: Simulation Kinetics of Aquation of $[Ru(NH_3)_5O_2CCH_2X]^{2+}$ (X=halogen)

The mechanism, kinetic rate constants, and activation parameters were estimated for the aquation reactions of $Ru(NH_3)_5X^{2+}$ (X=$FCH_2CO_2^-$, $ClCH_2CO_2^-$, $BrCH_2CO_2^-$, and $ICH_2CO_2^-$) by means of a computer simulation method with the iterative search technique. The aquation mechanism proposed first by Basolo *et al.* was found to be the best mechanism in which the protonated complexes play an important role as a quasi-stable intermediate. The order of aquation rates, iodoacetato$>$bromoacetato$>$chloroacetato$>$fluoroacetato, was well reflected in that of the activation energies for the rate-determining protonation process.

INTRODUCTION

In general, kinetic investigation of the reaction mechanism on the basis of the stationary-state method often finds difficulty in evaluating precise reaction rates for elementary reaction steps involving momentarily lived intermediates which play an important role in determination of reaction paths. In this respect, the computer simulation method with the iterative search technique for the estimation of rate constants has previously shown to be useful for discussing reaction mechanisms.[1]

Using the above simulation technique, the present authors report, here, on the aquation mechanism of a series of monohalogenoacetatopentaammineruthenium(III) complexes, $Ru(NH_3)_5X^{2+}$ (X=$FCH_2CO_2^-$, $ClCH_2CO_2^-$, $BrCH_2CO_2^-$, and $ICH_2CO_2^-$):

$$Ru(NH_3)_5X^{2+} + H_2O \xrightarrow{k_{obs}} Ru(NH_3)_5OH_2{}^{3+} + X^- \quad (1)$$

In regard to the aquation mechanism, Basolo *et al.*[2,3] have already proposed a mechanism involving a protonated intermediate in the aquation of acetato or substituted acetatopentaammine complexes of Co(III), Rh(III), and Ir(III). However, they did not show detailed kinetic evidences supporting their proposed mechanism. Therefore, the simulation analysis of the aquation mechanism for Reaction(1) seems of interest and significant.

EXPERIMENTAL

Materials and Kinetic Runs

Monohalogenoacetato- and aqua-pentaammineruthenium(III) complexes were prepared by the standard methods described in the previous papers.[4,5] All the kinetic experiments were carried out in a stoppered quartz cell placed in Shimazu UV 200 spectrophotometer under the conditions of $[Ru(NH_3)_5X^{2+}]_0$ (the subscript zero=initial state)=*ca.* 10^{-5} M, $[H^+]$=0.2 – 1.0 M, and the ionic strength (μ)=1.0 at 40 – 70°C. The proton concentration was adjusted by means of Toa HM–5A pH-meter and determined by the neutralization method. The ionic strength was adjusted with *p*-toluenesulfonic acid and its sodium salt, but it was not corrected according to the change in the proton concentration because, even in the high proton concentration, the protonation of *p*-toluenesulfonic acid was not marked enough to change the ionic strength considerably. The direct participation of the tosylate in the reaction mechanism as reactive species was then neglected. The aquation rate was followed by measuring the changes in the absorbances of the respective complex ion in the wavelength from 290 to 300 nm at appropriate intervals, as previously described.[6] The aqua-complex was separated and identified with the authentic sample according to the previous method,[6] and its concentration was determined by UV spectroscopic measurements.

RESULTS AND DISCUSSION

Overall Aquation Rate

In the previous investigations of the aquation reactions of acetato or substituted acetatopenta-ammine complexes of Co(III),[2,3] Rh(III),[3] and Ir(III),[3] the observed aquation rates (k_{obs}) have been found to be linearly dependent on the proton concentration, $[H^+]$. The linear dependency of the k_{obs} values for the $Ru(NH_3)_5X^{2+}$ (X=monohalogen-oacetato ligand) on $[H^+]$ was also found in the plots of k_{obs} *vs.* $[H^+]$ (Figure 1), and the rate constant k_{obs} can be separated into two terms:

$$k_{obs} = k_H[H^+] + k_{H_2O} \qquad (2)$$

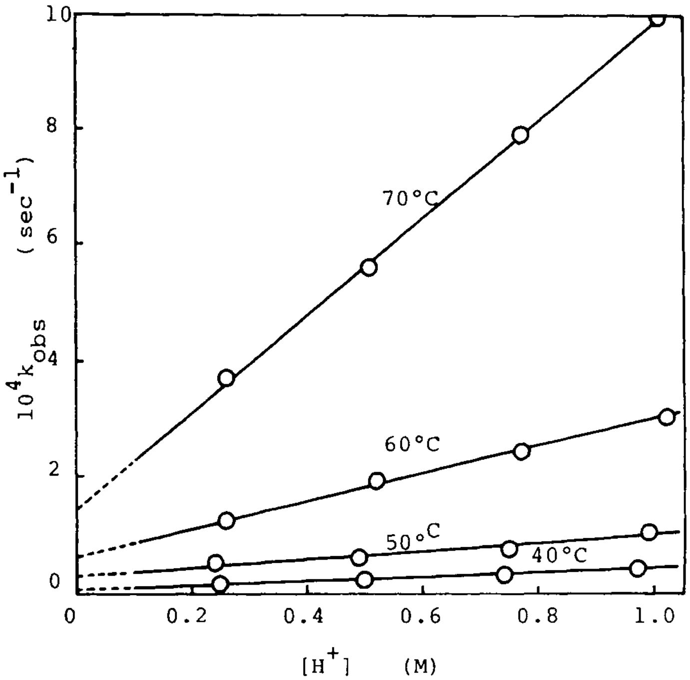


FIGURE 1 Plots of k_{obs} *vs.* $[H^+]$ for the $Ru(NH_3)_5O_2CCH_2Cl^{2+}$ aquation taken as a typical example.

The values of k_H and k_{H_2O}, those of which are proton-dependent and proton-independent rate constants respectively, are summarized in Table I, together with the activation parameters. The k_H and k_{H_2O} values and the activation parameters for the present $Ru(NH_3)_5X^{2+}$ aquation were not so much different from those for substituted acetatopentaammine complexes of Co(III), Rh(III), or Ir(III), and the overall activation energies for Reaction(1) indicated that the aquation proceeds more easily in the order of iodoacetato>bromoacetato>chloroacetato> -

TABLE I
Observed rate constants and activation parameters for Reaction(1)

X	$10^4 k_{obs}(sec^{-1})$				$10^5 k'_{H_2O}(sec^{-1})$				$10^3 k_H(M^{-1} sec^{-1})$			
	40°C	50°C	60°C	70°C	40°C	50°C	60°	70°C	40°	50°C	60°C	70°C
FCH_2CO_2 (I)	0.222	0.690	2.36	5.31	0.992	2.75	6.79	13.2	0.0246	0.083	0.355	0.798
$ClCH_2CO_2$ (II)	0.241	0.652	1.85	5.66	0.527	1.86	5.99	17.7	0.0440	0.077	0.238	0.842
$BrCH_2CO_2$ (III)	0.300	0.893	1.73	5.94	1.10	1.69	4.75	17.0	0.0382	0.145	0.251	0.847
ICH_2CO_2 (IV)	0.331	0.895	2.25	5.64	0.00	1.10	9.28	13.2	0.0696	0.157	0.264	0.864

X	E_a (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)	$\Delta H^{\ddagger}$ (kcal/mol)
(I)	22.9	− 8.85	22.3
(II)	22.5	−10.0	21.9
(III)	20.6	−15.7	20.0
(IV)	20.2	−16.9	19.5

fluoroacetato. This order apparently corresponds to the basicity order in the above monohalogenoacetate anions, and the basicity order *per se* seems to be directly related to that of the coordination strength of the Ru metal and the above basic ligand.

Aquation Mechanism

There are three reasonable aquation mechanisms (Mechanisms I, II, and III) which are able to satisfy the kinetic relationship given by Eq. (2). Mechanism I involves the protonated complexes, $Ru(NH_3)_5XH^{3+}$, as a quasi-stable intermediate:

$$Ru(NH_3)_5X^{2+} + H_2O \underset{k_1}{\overset{k_{H_2O}}{\rightleftharpoons}} Ru(NH_3)_5OH_2{}^{3+} + X^- \tag{3a}$$

$$Ru(NH_3)_5X^{2+} + H^+ \underset{k_2}{\overset{k_H}{\rightleftharpoons}} Ru(NH_3)_5XH^{3+} \tag{3b}$$

$$Ru(NH_3)_5XH^{3+} + H_2O \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Ru(NH_3)_5OH_2{}^{3+} + HX \tag{3c}$$

where k_1 and k_4 can be neglected when $[X^-]_0=0$.

The stationary-state assumption for $[Ru(NH_3)_5XH^{3+}]$ gives the following relation:

$$k_{obs} = k'_H k'_3 + (k_1 k_2 + k_2 k'_4 + k_1 k'_3) [X^-] / (k_2 + k'_3) + k'_{H_2O} \tag{4}$$

where $k'_H(=k_H[H^+])$, $k'_3(=k_3[H_2O])$, $k'_4(=k_4[H^+])$, and $k'_{H_2O}(=k_{H_2O}[H_2O])$ are pseudo-first-order rate constants. Eq. (4) reduces to Eq. (2) under $k_2 \ll k'_3$ and $[X^-]_0=0$.

Mechanism II is a S_N2 mechanism combined with a S_N1 reaction in which a five-coordinate intermediate is considered to be formed from the dissociation of the protonated complex:

$$Ru(NH_3)_5X^{2+} + H_2O \underset{k_6}{\overset{k_5}{\rightleftharpoons}} Ru(NH_3)_5OH_2{}^{3+} + X^- \tag{5a}$$

$$Ru(NH_3)_5X^{2+} + H^+ \xrightarrow{fast} [Ru(NH_3)_5XH^{3+}] \underset{k_8}{\overset{k_7}{\rightleftharpoons}} Ru(NH_3)_5{}^{3+} + HX \tag{5b}$$

$$Ru(NH_3)_5{}^{3+} + H_2O \underset{k_{10}}{\overset{k_9}{\rightleftharpoons}} Ru(NH_3)_5OH_2{}^{3+} \tag{5c}$$

where k_6 and k_8 are negligible under $[X^-]_0=0$.

The remained mechanism (Mechanism III) includes a formation of the five-coordinate intermediate *via* a heterolytic dissociation of $Ru(NH_3)_5X^{2+}$ by H_2O without the direct displacement of the X^-ligand with H_2O through the S_N2 reaction:

$$Ru(NH_3)_5X^{2+} \underset{k_{12}}{\overset{k_{11}, H_2O}{\rightleftharpoons}} Ru(NH_3)_5{}^{3+} + X^- \tag{6a}$$

$$Ru(NH_3)_5X^{2+} + H^+ \xrightarrow{fast} [Ru(NH_3)_5XH^{3+}] \underset{k_{14}}{\overset{k_{13}}{\rightleftharpoons}} Ru(NH_3)_5{}^{3+} + HX \tag{6b}$$

$$Ru(NH_3)_5{}^{3+} + H_2O \underset{k_{16}}{\overset{k_{15}}{\rightleftharpoons}} Ru(NH_3)_5OH_2{}^{3+} \tag{6c}$$

where k_{12} and k_{14} can also be discarded when $[X^-]_0=0$. Both of Mechanisms II and III are capable of satisfying the kinetic relationship of Eq. (2) under $k_7=k_{13}=k'_H$, $k_5=k_{11}=k_{H_2O}$, and $[X^-]_0=0$.

In addition to Mechanisms I, II, and III, another aquation mechanisms which include $Ru(NH_3)_5XH^{3+}$, $Ru(NH_3)_5{}^{3+}$, or seven-coordinate intermediate $[Ru(NH_3)_5XH(OH_2)]^{3+}$ can also be considered, but they did not offer reasonable kinetic relations in terms of their coincidence with the relationship expressed by Eq. (2).

In order to select the best mechanism, the non-stationary-state analysis was then performed on Mechanisms I, II, and III by means of the simulation technique.[1] The simulation with roughly estimated k_2 $(=k_{10}=k_{16})$ and k'_3 $(=k'_9=k'_{15})$ values in their one significant figure and the experimentally determined k'_H $(=k_7=k_{13})$ and k'_{H_2O} $(=k'_5=k'_{11})$ under the conditions of $k_1=k_4=k_6=k_8=k_{12}=k_{14}=0$ (viz., $[X^-]_0=0$) resulted in indistinguishable time-conversion curves of $[Ru(NH_3)_5X^{2+}]$ or $[Ru(NH_3)_5OH_2{}^{3+}]$ for Mechanisms I, II, and III (for example, see the $Ru(NH_3)_5O_2CCH_2Cl^{2+}$ aquation at 60°C in Figure 2). Since the almost identical time-conversion

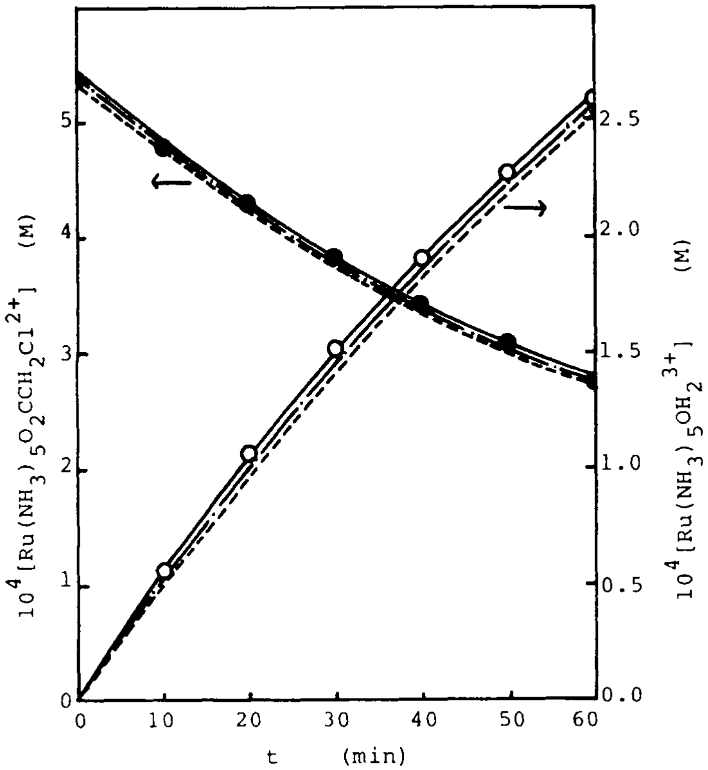


FIGURE 2 Time conversions of $[Ru(NH_3)_5O_2CCH_2Cl^{2+}]$ and $[Ru(NH_3)_5OH_2{}^{3+}]$ in the $Ru(NH_3)_5O_2CCH_2Cl^{2+}$ aquation at 60°C. Circle point (observed result); ——— (Mechanism I), — — —— (Mechanism II), and — — — — (Mechanism III) simulated with $k_H = k_7 = k_{13} = 2.38 \times 10^{-4}\ M^{-1}\ sec^{-1}$, $k'_{H_2O} = k'_5 = k'_{11} = 5.99 \times 10^{-5}\ sec^{-1}$, $k_2 = k_{10} = k_{16} = 10^{-3}\ sec^{-1}$, $k'_3 = k'_9 = k'_{15} = 1\ sec^{-1}$, and $k_1 = k_4 = k_6 = k_8 = k_{12} = k_{14} = 0$.

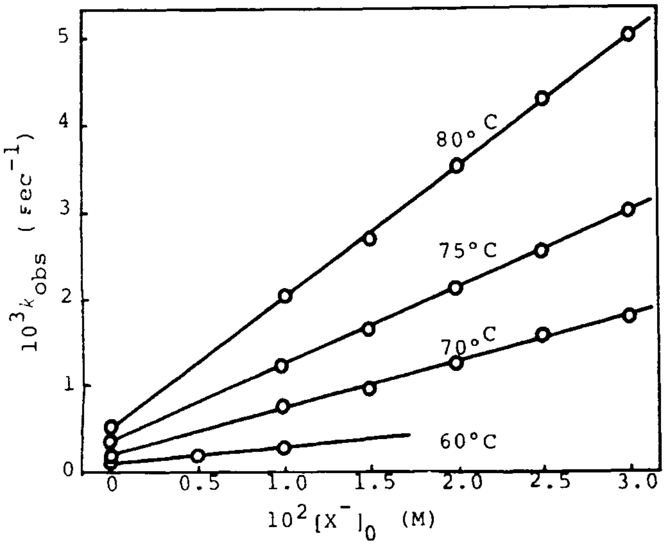
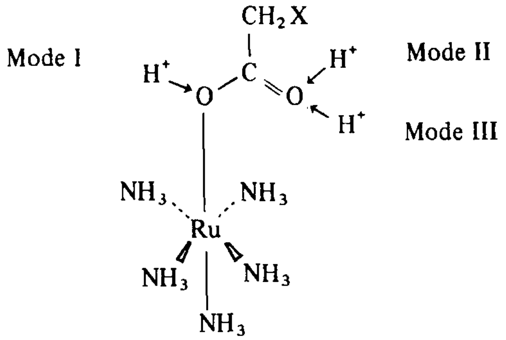


FIGURE 3 Plots of k_{obs} vs. $[X^-]_0$ for the $Ru(NH_3)_5CCH_2Cl^{2+}$ aquation (pH = 2.0 and μ = 1.0) taken as a typical example.

curves were not separated between Mechanisms I, II, and III by the change in the concentrations of the proton and the reactant, the concentration effect of the monohalogenoacetate ions will be taken into consideration for the selection of the most plausible mechanism. The overall aquation rates showed a first-order dependence on the initial X^- concentrations (Figure 3), and such a first-order dependence can always be expected only from Eq. (4) obtained for Mechanism I. Therefore, Mechanism I seems most preferable, and the protonated complex is closed up as an important intermediate.

Protonated $Ru(NH_3)_5XH^{3+}$ *Intermediate*

The protonated complex formations can be expected from the following three possible interactions between $Ru(NH_3)_5X^{2+}$ and H^+:



All the above modes commonly represent the interaction between the oxygen lone-pair 2*p*-orbitals and the hydrogen *s*-orbital. The extended Hückel calculations[7] on a simple model of the interaction between $Ru(NH_3)_5O_2CH^{2+}$ and H^+ resulted in the largest stabilization energy (4.46 eV) for Mode I, giving a maximum magnitude of the weakness in the bond strength of the Ru–O linkage. However, *the heterolytic dissociation of the Ru–O linkage by the protonation seems to be hardly expected, because the protonation weakens the Ru–O bond strength in a magnitude of ca. 10% of that of the parent species.* That is, the protonation decreases the bond population of the Ru–O linkage in a magnitude of *ca.* 10% in Mode I, so that the large stabilization energy obtained by the protonation of the complex may favor the presence of the protonated complex as a quasi-stable intermediate in the aquation reaction.

Rate Constant Estimation

From the discussions made above, Mechanism I was

TABLE II
Estimated rate constants

X	$10^2 k_2$ (sec^{-1})				k'_3 (sec^{-1})			
	40°C	50°C	60°C	70°C	40°C	50°C	60°C	70°C
(I)	0.49	0.81	1.3	2.0	0.51	0.80	1.2	1.8
(II)	0.072	0.15	0.29	0.55	0.87	0.92	0.97	1.0
(III)	0.17	0.57	1.8	5.5	1.8	2.3	2.8	3.4
(IV)	0.18	0.45	1.1	2.4	0.59	1.2	2.5	4.8

found to be the most plausible one which involves four unknown rate constants in addition to the experimentally determined k_H and k_{H_2O}. The estimation of k_2 and k'_3 values was, then, performed under $[X^-]_0=0$ (*viz.*, $k_1=k_4=0$) for a shortage of computation time, and the estimated k_2 and k'_3 values in their two significant figures are summarized in Table 2. The estimated values for the above rate constants seem reliable in view of the satisfactory accordance between the onserved and simulated time conversions of $[Ru(NH_3)_5X^{2+}]$ and $[Ru(NH_3)_5OH_2{}^{3+}]$; this is indicated in Figure 4, taking the $Ru(NH_3)_5O_2CCH_2Cl^{2+}$ aquation as an example.

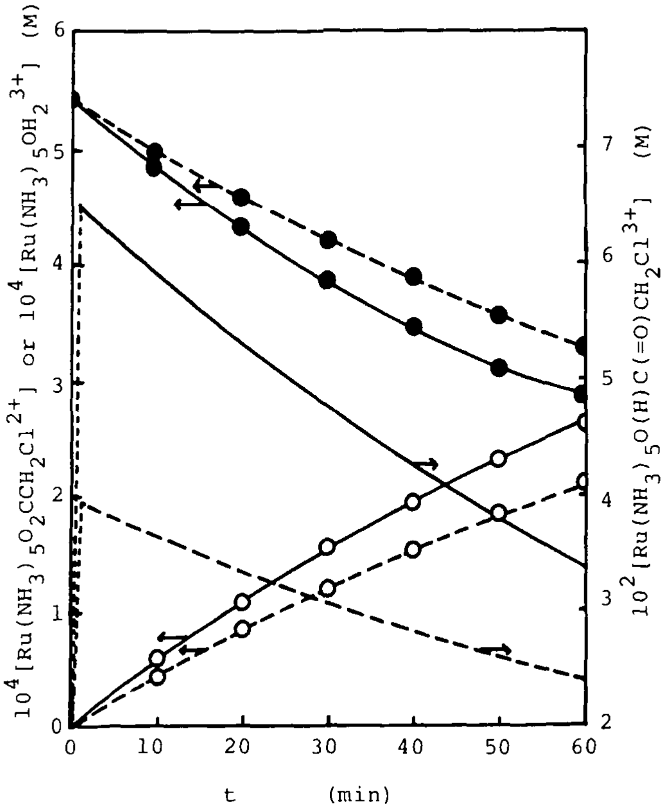


FIGURE 4 Computer simulation of the $Ru(NH_3)_5O_2CCH_2Cl^{2+}$ aquation at 60°C with the estimated rate constants under two different $[H^+]$: Circle point = observed result; solid curve = simulation for $[H^+]$ = 0.5 M; dotted curve = simulation for $[H^+]$ = 0.3 M.

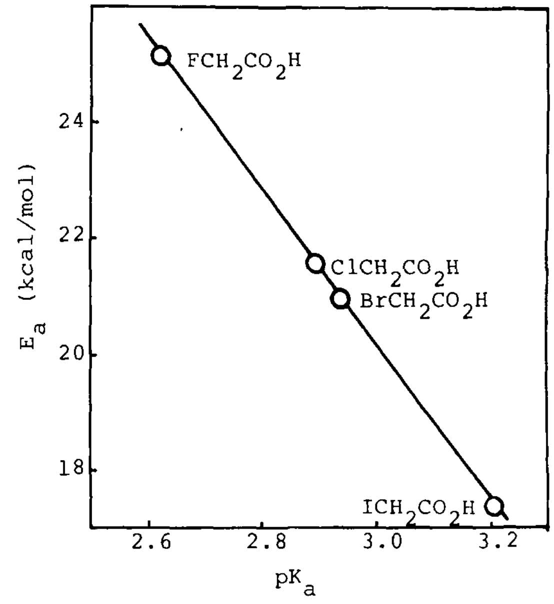


FIGURE 5 Plots of the E_a values for the protonation process (Reaction (6b)) *vs.* the pK_a values for monohalogenoacetic acids.

Although the dissociation of the proton from the protonated complex in Reaction(3b) is faster than the protonation, the remarkably fast reaction of the nucleophilic displacement of H_2O with the protonated ligand in Reaction (3c) makes the formation of the aqua-complex favorable, and, in fact, the activation energy of this aquation process in Reaction(3c) is markedly small as compared with those of the other processes (Table III). This is owing to an energetically favorable interaction between the lowest-unoccupied $d_{z^2}(Ru)$–$p_z(O)$ antibonding

TABLE III
Activation parameters for the elementary steps

	Reaction(3a)			Reaction(3b)						Reaction(3c)		
	Forward			Forward			Backward			Forward		
X	E_a	$\Delta S^\ddagger$	$\Delta H^\ddagger$	E_a	$\Delta S^\ddagger$	$\Delta H^\ddagger$	E_a	$\Delta S^\ddagger$	$\Delta H^\ddagger$	E_a	$\Delta S^\ddagger$	$\Delta H^\ddagger$
(I)	18.5	-24.6	17.8	25.2	- 1.30	24.6	10.1	-43.8	9.41	9.02	-33.3	8.37
(II)	25.0	- 4.97	24.4	21.6	-12.3	20.9	14.4	-33.7	13.8	1.11	-57.5	0.457
(III)	20.1	-19.9	19.4	21.0	-13.6	20.4	24.9	1.45	24.2	4.50	-45.2	3.85
(IV)	26.9	0.408	26.2	17.4	-24.5	16.7	18.5	-18.7	17.9	14.9	-14.1	14.3

Units are the same as in Table I.

orbital on the protonated complex and the highest-occupied lone-pair oxygen 2*p*-orbital on H_2O; namely, the nucleophilic attack of H_2O increases the antibonding nature of the Ru–O linkage in the protonated complex so as to dissociate the Ru–O bond heterolytically. It is also noteworthy that the overall activation energies of Reaction(1), which follow the order of iodoacetato>bromoacetato>-chloroacetato>fluoroacetato, were well reflected in those of the rate-determining protonation process in Reaction(3b).

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7. The diagonal H_{ii} terms were taken to be *d*(12.0eV), *s*(9.0eV), and *p*(7.0eV) for Ru atom, and those for the other atoms (H, C, N, and O) were supplied from J. Hinze and H. H. Jaffe, *J. Amer. Chem. Soc.*, **84**, 540 (1962). The off-diagonal H_{ij} terms were evaluated by $H_{ij}=1.75(H_{ii}+H_{jj})S_{ij}/2$, where S_{ij} is the overlap integral between the i-th and j-th AOs. The geometry of $Ru(NH_3)_5O_2CH^{2+}$ were taken to be Ru–O=2.5 Å, Ru–N=2.33 Å, N–H=1.031 Å, N–Ru–N=90°, Ru–O–C angle=105°, C–O=1.36 Å, C=O=1.23 Å, O–C–O angle=122.4°, O–C–H angle=118.8°, and $O-H^+=0.96$ Å. The EHMO calculations resulted in satisfactorily good excitation energy of 27.5 kK (exptl.=24.9 kK) and 10 Dq value of 5.35 kK (exptl.=*ca.* 4 kK estimated from the Dq(=2.10 kK) of the first series metal complexes).