Studies on the Ruthenium Complexes. IX.[1] Kinetic Studies on the Deaquation-anation Reaction of Aquapentaammineruthenium(III) Complexes[2]

Akira Ohyoshi, Shun-ichi Hiraki, Tomio Odate, Susumu Kohata, and Junko Oda
Department of Industrial Chemistry, Faculty of Engineering, University of Kumamoto, Kumamoto 860

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The deaquation-anation reaction of $[Ru(OH_2)(NH_3)_5]X_3$-type complexes in the solid state, as shown by the $[Ru(OH_2)(NH_3)_5]X_3(s) \rightarrow [RuX(NH_3)_5]X_2(s) + H_2O(g)$ equation, where X is Cl, Br, I, and NO_3 respectively, was kinetically studied by means of thermogravimetry (TG) along with differential thermal analysis (DTA). The activation energy and entropy in the reaction process (E_a kcal/mol, $\Delta S^{\neq}$ e.u.) are, respectively, found by isothermal kinetic study to be (22.7, −7.1) for the chloride, (23.4, −5.2) for the bromide, (26.7, 5.8) for the iodide, and (19.3, −15.9) for the nitrate. The reaction seems to proceed through the following two steps, except in the case of the iodide: $[Ru(OH_2)(NH_3)_5]X_3 \rightarrow [RuX(OH_2)(NH_3)_5]X_2 \rightarrow [RuX(NH_3)_5]X_2 + H_2O$. The first step is regarded as the rate-determining one.

Several kinetic studies on the deaquation-anation of cobalt(III)[3-6] and chromium(III)[7-9] pentaammine complexes in the solid state have been made, and the reaction heats have been reported. These metal ions have six and three 3d-electrons respectively, while ruthenium(III) has five 4d-electrons. This difference in the electronic structure of the central metal ion may be reflected in the behavior of the deaquation-anation reaction. In the present paper, the results of the deaquation-anation study of several aquapentaammineruthenium(III) complexes in the solid state will be compared with those of the corresponding cobalt(III) and chromium(III) complexes and the reaction mechanisms will be discussed.

Experimental

Materials. The aquapentaammineruthenium(III) complexes were prepared from the chloropentaammineruthenium(III) chloride by the method of Endicott and Taube.[10] The complexes were studied immediately after identification because they were unstable with respect to deaquation, even at room temperature. The water contents of the complexes were determined by studying the mass-loss on a thermobalance. Found for the chloride: H_2O, 5.55%. Calcd for $[Ru(OH)_2(NH_3)_5]Cl_3$: H_2O, 5.79%. Found for the bromide: H_2O, 3.37%. Calcd for $[Ru(OH_2)(NH_3)_5]Br_3$: H_2O, 3.37%. Found for the iodide: H_2O, 2.84%. Calcd for $[Ru(OH_2)(NH_3)_5]I_3$: H_2O, 3.08%. Found for the nitrate: H_2O, 4.22%. Calcd for $[Ru(OH_2)(NH_3)_5](NO_3)_3$: H_2O, 4.11%. Since there were some differences between the observed and theoretical values, and since this measurement was difficult to do for the perchlorate, the absorption spectrophotometry was also carried out in order to identify these complexes and to confirm their chemical purity.

Procedures. A Shimadzu-TGC 20 micro-thermobalance and DT 20B micro differential thermal analyzer were used for the thermal analysis. A Hitachi 323 recording spectrophotometer was used for the spectrum measurements.

About a 8—10 mg sample was heated in a dynamic helium atmosphere in a furnace at a heating rate of 5 °C per min. The isothermal rate measurement was carried out by using a thermobalance at several constant temperatures, and the conversion ratios were determined by mass-loss measurements. The reaction products were spectrophotometrically analyzed for their aqueous solution.

Results and Discussion

Differential Thermal Analysis and Thermogravimetry. The DTA and TG curves recorded for the aquapentaammine halides, nitrate, and perchlorate are shown in Fig. 1. For each complex, the mass-loss step, as shown by the TG curve, corresponds to the endothermic or exothermic peak in the temperature range of 62→81(max)→92 °C for the chloride, in that of 67→78(max)→91 °C for the bromide, in that of 58→76(max)→96 °C for the iodide, in that of 56→73(max)→83 °C for the nitrate, and in that of 127→156(max)→170 °C for the perchlorate. The DTA curve of perchlorate shows an exothermic peak different from those of the other complexes. This suggests that the ligand water-molecule is maintained even at a comparatively high temperature, since the bulky perchlorate ion can not easily migrate toward the inner sphere. This fact seems to account for the mechanism by which the

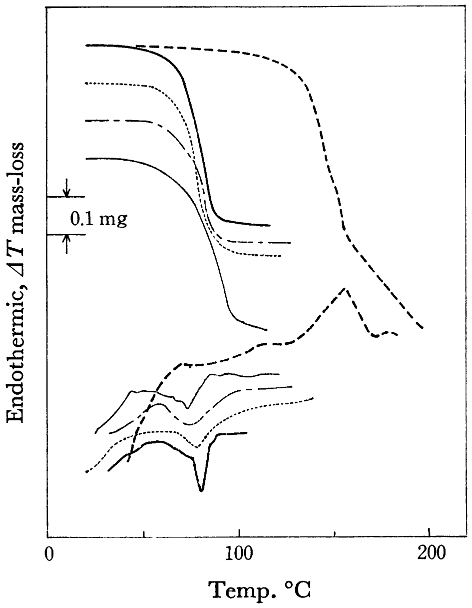

Fig. 1. TG and DTA curves of $[Ru(OH_2)(NH_3)_5]X_3$ complexes.
—— Chloride, ······ Bromide, —·— Iodide,
—— Nitrate, ---- Perchlorate.

Table 1. Analysis of the reaction product of aquapentaammineruthenium(III)

Initial complex		Chloride	Bromide	Iodide	Nitrate
Sampling temp. °C		92	91	96	83
Sample color		Yellow	Orange	Black	Gray
Chemical formula assigned		$[RuCl(NH_3)_5]Cl_2$	$[RuBr(NH_3)_5]Br_2$	$[RuI(NH_3)_5]I_2$	$[Ru(NO_3)(NH_3)_5](NO_3)_2$
Elemental analysis (H%, N%)	Found	(5.24, 23.65)	(3.90, 16.80)	(2.69, 12.03)	(3.96, 29.05)
	Calcd	(5.18, 23.93)	(3.56, 16.44)	(2.67, 12.35)	(4.06, 30.24)
Electronic spectrum (ν_{max}, kK, ε, 10^3 M^{-1}, cm^{-1})	Found	(31, 1.95)	(25, 1.52)	(18, 2.15)	(34, —)[b]
	Ref.[c]	(30, 1.94)	(25, 1.95)	(18, 2.10)	(—, —)

a) Electronic spectrum was measured as a dilute nitric acid solution. b) Unstable in aqueous solution.
c) From Ref. 11.

deaquation reaction is initiated by the migration of the outersphere anion.

The results of the elemental analysis and the spectral data of the reaction products are shown in Table 1. These data indicate that the reaction products accord with those of complexes resulting from the ligand-exchange reactions between the ligand water-molecule and the outersphere anions. Thus, all the peaks on the DTA curves and the mass-loss are attributable to the deaquation-anation reactions;

$$[Ru(OH_2)(NH_3)_5]X_3(s) \longrightarrow [RuX(NH_3)_5]X_2(s) + H_2O(g). \quad (1)$$

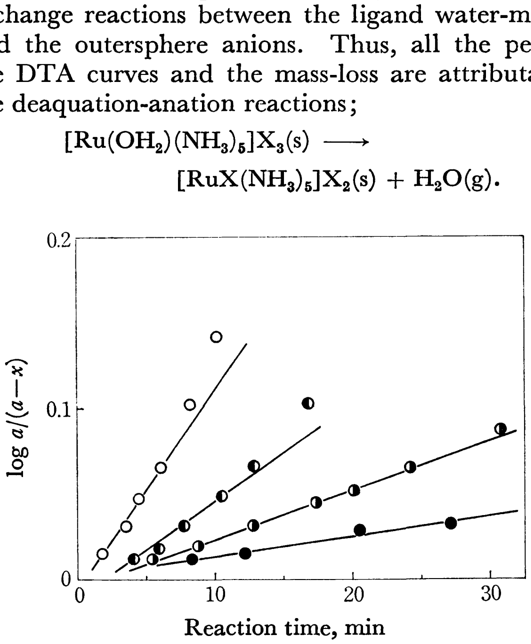

Fig. 2. Plots of log $a/(a-x)$ vs. reaction time for the deaquation-anation reaction of $[Ru(OH_2)(NH_3)_5]Cl_3$.
—●— 41 °C, —◑— 49 °C, —◐— 55 °C,
—○— 63 °C.

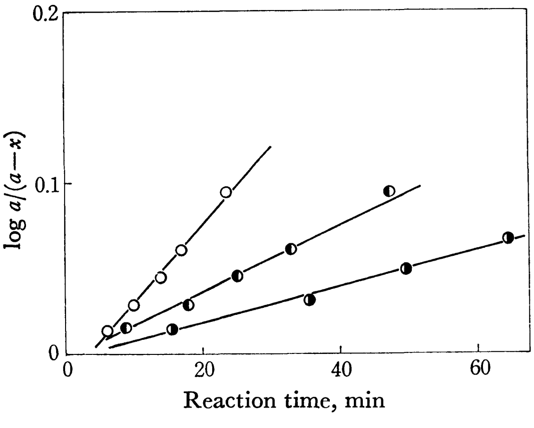

Fig. 3. Plots of log $a/(a-x)$ vs. reaction time for the deaquation-anation reaction of $[Ru(OH_2)(NH_3)_5]I_3$.
—◑— 35 °C, —◐— 40 °C, —○— 46 °C.

Isothermal Kinetic Study. Since the thermochemical reactions of all complexes except for the perchlorate were observed to consist of the deaquation and anation of the outersphere anion, the isothermal kinetic measurements were made using a thermobalance. The changes in the conversion ratios were determined from the mass-loss data at several temperatures. The plots of log $a/(a-x)$ vs. the reaction time, t, are exemplified for the chloride and the iodide in Figs. 2 and 3 respectively, where "a" is the initial mass of the sample and "$a-x$" is the mass at time t. The rate was considerably accelerated as the reaction proceeded, and the plots showed a tendency to deviate from the straight lines at higher reaction temperatures. Similar trends have previously been reported for the cases of the bromide and the nitrate.[2] The rate constants and the activation energies (E_a-I), which are obtained from the Arrhenius plots (Fig. 4), are given in Table 2, along with the activation entropy calculated from the E_a—I value and along with the reference values. Kinetic plots calculated by the method of Freeman and Carroll[12] are shown in Fig. 5, while the activation energies (E_a-II) are also listed in Table 2.

It can be seen that the rate constants for the ruthenium(III) complexes are larger than those of the cobalt(III) and chromium(III) complexes, and that the activation energies for the reactions of the ruthenium(III) complexes are generally smaller than those

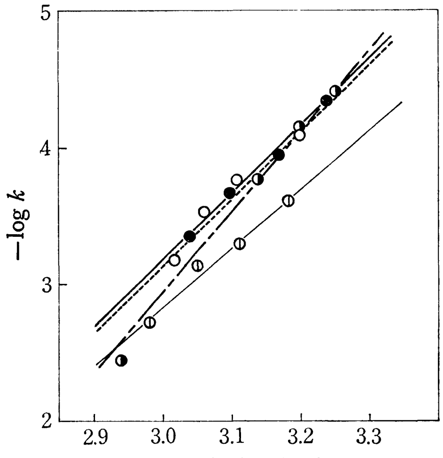

Fig. 4. Arrhenius plots for the deaquation-anation reaction of $[Ru(OH_2)(NH_3)_5]X_3$ complexes.
—●— Chloride, —○— Bromide, —◑— Iodide,
—⦶— Nitrate.

TABLE 2. KINETIC PARAMETERS FOR THE DEAQUATION-ANATION REACTION OF $[M(OH_2)(NH_3)_5]X_3$ TYPE COMPLEXES

Complexes	k, 10^4 s^{-1} (Temp., °C)	E_a-I (kcal/mol)	E_a-II (kcal/mol)	$\Delta S^{\neq}$ (e.u.)	Temp.[a] (°C)	Anionic radii[b] and proton affinities[c] (Å)	(kcal/mol)
$[Ru(OH_2)(NH_3)_5]Cl_3$	1.12 (43)	22.7	24.6	−7.1	31	1.81	331
$[Ru(OH_2)(NH_3)_5]Br_3$	0.77 (40)	23.4	26.8	−5.2	40	1.96	321
$[Ru(OH_2)(NH_3)_5]I_3$	0.71 (40)	26.7	32.6	5.8	38	2.20	312
$[Ru(OH_2)(NH_3)_5](NO_3)_3$	2.38 (41)	19.3	19.0	−15.9	30	1.89	—
$[Ru(OH_2)(NH_3)_5](ClO_4)_3$	—	—	—	—	48	2.36	—
$[Co(OH_2)(NH_3)_5]Cl_3$	4.27 (86)[d]	19[d]	—	—	40[d]		
$[Co(OH_2)(NH_3)_5]Br_3$	4.79 (85)	25	—	—	80		
$[Co(OH_2)(NH_3)_5]I_3$	—	—	—	—	70		
$[Co(OH_2)(NH_3)_5](NO_3)_3$	2.51 (85)	31	—	—	50		
$[Cr(OH_2)(NH_3)_5]Cl_3$	2.41 (65)[e]	25,[f] 26.4[g]	28[h]	−2.53[e]	60[h]		
$[Cr(OH_2)(NH_3)_5]Br_3$	2.43 (76)	36, 29.7	38	9.2	68		
$[Cr(OH_2)(NH_3)_5]I_3$	1.61 (82)	19, 32.7	—	15.4	70		
$[Cr(OH_2)(NH_3)_5](NO_3)_3$	1.38 (55)	14, 24.3	18	−2.49	40		

a) Temp. of mass-loss initiation. b) From Ref. 13. c) From Ref. 14 for X^-. d) From Ref. 5. e) From Ref. 9. f) Obtained by DTA in Ref. 8. g) $\Delta H^{\neq}$ in Ref. 9. h) From Ref. 8.

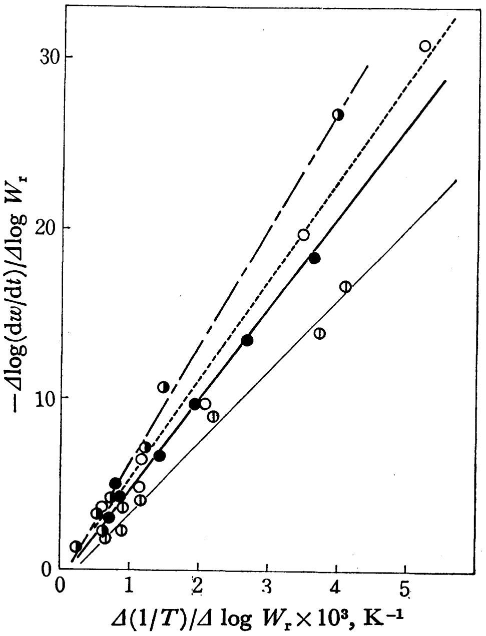

Fig. 5. The application of Freeman-Carroll Equation to the deaquation-anation reaction of $[Ru(OH_2)(NH_3)_5]X_3$ complexes.
—●— Chloride, —○— Bromide, —◑— Iodide, —⦶— Nitrate.

for the corresponding cobalt(III) complexes. This is attributable to the presence of a lower unoccupied t^6_{2g} d-orbital for the ruthenium(III) ion and to the great softness of the 4d transition metal. The effects of the outer sphere anion on the thermal stability of the aquapentaammine complex are somewhat complicates. If the temperature of the mass-loss initiation indicates the thermal stability of a complex, this order is in agreement with that of the increase in the ionic radius and that of the decrease in the nucleophilic affinity, which is conveniently shown by the proton affinity in Table 2. The nitrate gives the largest value of the rate constant for the deaquation-anation reaction of the aquapentaammineruthenium(III), while it gives the smallest value for the cobalt(III) aquapentaammine complex. For the ruthenium complexes, the relation between the rate constant and the activation energy is generally consistent; that is, the larger rate constant corresponds to the smaller activation energy value. The activation entropy values are generally small and negative, except for the iodide. This means that the aquapentaammine complex has less randomness in the activated state and that, therefore, the deaquation-anation probably takes the S_N2 mechanism. On the other hand, the reaction may have a S_N1-like mechanism for the iodide.

Reaction Mechanism of the Deaquation-anation. Considering the reaction mechanism, it is convenient to divide Reaction (1) into two kinds of reaction schemes, 2—3 or 4—5:

$$[Ru(OH_2)(NH_3)_5]X_3 \longrightarrow [Ru(NH_3)_5]X_3 + H_2O \tag{2}$$

$$[Ru(NH_3)_5]X_3 \longrightarrow [RuX(NH_3)_5]X_2 \tag{3}$$

and

$$[Ru(OH)_2(NH_3)_5]X_3 \longrightarrow [RuX(OH_2)(NH_3)_5]X_2, \tag{4}$$

$$[RuX(OH_2)(NH_3)_5]X_2 \longrightarrow [RuX(NH_3)_5]X_2 + H_2O. \tag{5}$$

If Reaction Path 2 is the rate-determining step, the activation energies in all the cases of deaquation-anation reactions should be approximately close to each other. When the rate of the anation process (4) is smaller than that of the deaquation process (5), the deaquation-anation reaction is a S_N2-type mechanism. The experimental results shown in Table 2 support this reaction mechanism. As is also shown in Table 2, the rate constant for the nitrate is nearly two or three times larger than those for the other complexes and the activation energies for the latter are about 1.3—1.7 times that for the nitrate. This suggests that the deaquation-anation reaction takes place through

Reactions 4 and 5, that is the S_N2 mechanism. These relations are in agreement with that predicted from the crystal-field activation energy,[15] assuming a seven-coordinated intermediate in the reaction corresponding to Reaction 4. Moreover, the reaction in the solid state will be more likely to take the S_N2 mechanism than that in the aqueous phase, because the outersphere anion may be fixed by the lattice energy at the position neighboring the innersphere ligand in the solid state.

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