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DEAQUATION-ANATION REACTION OF AQUOPENTAAMMINERUTHENIUM(III) COMPLEXES

Akira OHYOSHI, Shunichi HIRAKI, Tomio ODATE, and Susumu KOHATA
Department of Industrial Chemistry, Faculty of Engineering,
Kumamoto University, Kurokami, kumamoto 860

The deaquation-anation reaction of $[Ru(H_2O)(NH_3)_5]X_3$ type complexes in solid state, as shown by the equation, $[Ru(H_2O)(NH_5)_5]X_3$ (s) → $[RuX(NH_3)_5]X_2$ (s) + H_2O (g), where X=NO_3 and Br was investigated by means of the differential thermal analysis (DTA) and of the thermogravimetry (TG). The activation energies in the deaquation-anation processes of the nitrate and bromide were calculated as 17.5 and 23.0 kcal/mol by the isothermal rate study, and as 19.0 and 26.8 kcal/mol by the Freeman-Carroll analysis.

The heats of deaquation-anation of cobalt(III) pentaammines[1-4] and chromium(III) pentaammines[5,6] in solid state have already been reported. These metal ions have six and three 3d-electrons, while ruthenium(III) has five 4d-electrons. Therefore, it is of interest to study the deaquation-anation of a similar type of ruthenium(III) complexes and to compare it with that of the corresponding cobalt(III) and chromium(III) complexes. In this paper, we will describe on the results of deaquation-anation study of aquopentaammineruthenium(III) nitrate and bromide in solid state, and the reaction mechanisms are discussed.

Aquopentaammineruthenium(III) nitrate and bromide were prepared by the method of Endicott and Taube.[7] The compounds were studied immediately after preparation and analysis since they were unstable with respect to deaquation even at room temperature. Water contents of the compounds were determined by mass-loss on a thermobalance. Found: H_2O, 4.61%. Calcd for $[Ru(H_2O)(NH_3)_5](NO_3)_3$: H_2O, 4.22%. Found: H_2O, 3.37%. Calcd for $[Ru(H_2O)(NH_3)_5]Br_3$: H_2O, 4.06%. Since there were some differences between observed values and theoretical values, the purities of compounds were also checked by the absorption spectrophotometry.

A Shimadzu-T.G.C.20 micro-thermobalance, -D.T.20B micro-differential thermal analyzer, -LM type micro-balance, and -UV 200 spectrophotometer were used for the experiments.

About 8-10 mg sample was pyrolyzed in a dynamic helium atmosphere in a furnace with heating rate of 5° per minute. The isothermal rate measurement was carried out by using a thermobalance at several constant temperatures, and the conversion ratios were determined by the mass-loss measurement. Intermediate and final products were spectrophotometrically checked for their aqueous solutions.

The DTA and TG curves, recorded for the aquopentaammine nitrate (A) and bromide (B) are shown in Fig.1. For each compound, the first dropping of the TG curve corresponds to the appearance of endothermic peak at the temperature range of 56°→73°(max)→83° for nitrate and at the range of 67°→78°(max)→91° for bromide. The absorption spectra of the solution of the sample obtained at 83°C for the former compound and at 91°C for the

latter are in agreement with those of the nitrato and bromo complexes respectively. Thus, the endothermic peaks and the mass-loss curves at above described temperatures could be attributable to the changes corresponding to the deaquation-anation reactions.

i.e., $[Ru(H_2O)(NH_3)_5]X_3$ (s) → $[RuX(NH_3)_5]X_2$ (s) + H_2O (g) (1)

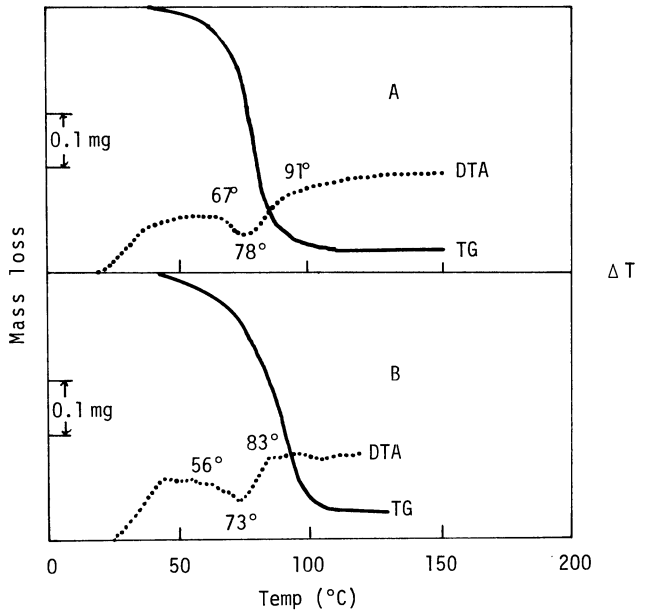

Fig.1. DTA and TG curves of $[Ru(H_2O)(NH_3)_5]X_3$
A:X=NO_3, B:X=Br

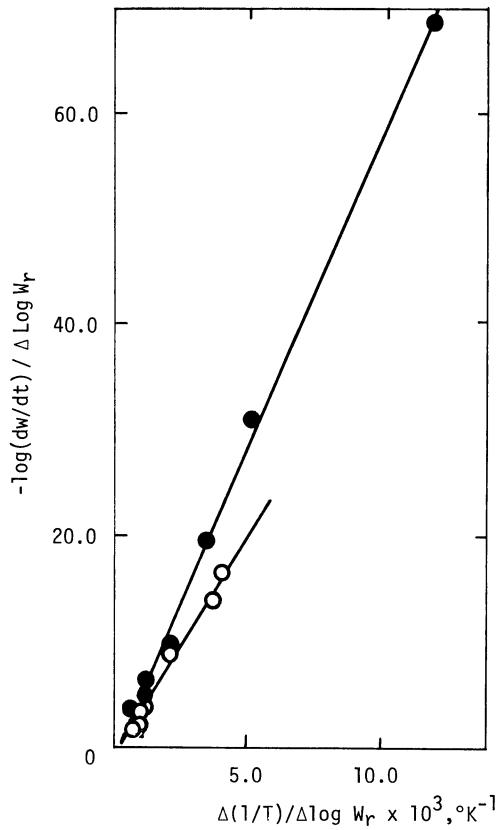

Fig.2. The plots of Freeman-Carroll equation for the reaction, $[Ru(H_2O)(NH_3)_5]X_3$ → $[RuX(NH_3)_5]X_2 + H_2O$, X=NO_3(o), X=Br(●).

Since the thermochemical reactions of both complexes were observed to consist of deaquation and anation of outer sphere anion, the kinetic treatment was made by the method of Freeman and Carroll.[8] These kinetic plots are shown in Fig.2 and the activation energies (E_a-I) are listed in Table 1.

The isothermal kinetic measurement was made using a thermobalance. The changes of the conversion ratios were determined from the mass-loss data at several temperatures. The plots of log a/(a-x) vs. reaction time t are shown in Fig.3, where "a" is the initial mass of sample, and "a-x" is the mass at time t. As is shown in Fig.3, the rate was considerably accelerated as the reaction proceeded and the plots showed a tendency of deviation from the straight lines at higher reaction temperatures. The first-order rate constants were determined from initial slopes of the plots of log a/(a-x) versus t at various temperatures. The rate constants and the activation energies (E_a-II), which are obtained from the Arrhenius plots, are given in Table 1 along with those of the reference reactions. It can be seen that the rate constants for ruthenium(III) complexes are 10∿43 fold larger than those of cobalt(III) complex bromide and nitrate. The activation energies for the ruthenium(III) and chromium(III) complex bromides are larger than those

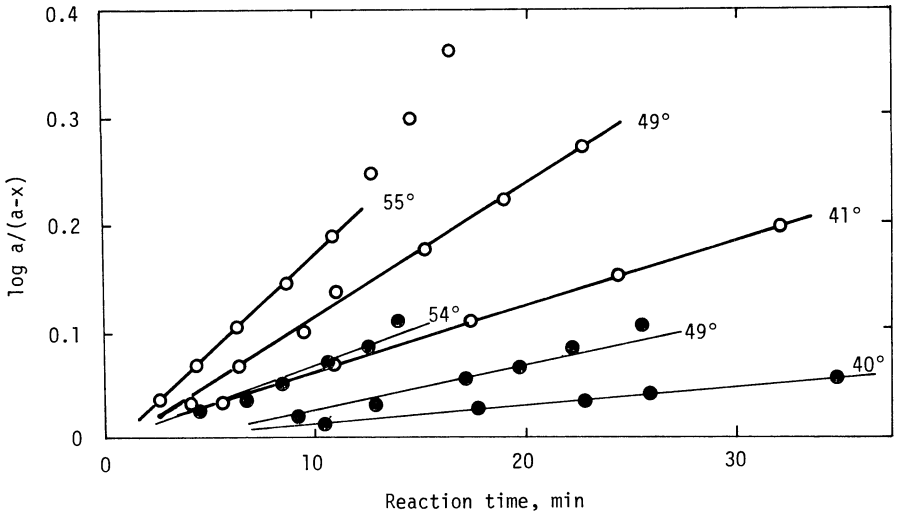

Fig.3. The relationships of log a/(a-x) against reaction time for deaquation-anation of $[Ru(H_2O)(NH_3)_5]X_3$, X=NO_3(o), X=Br(●).

Table 1. Rate Constants and Activation Energies of Deaquation-Anation Reactions of $[M(H_2O)(NH_3)_5]X_3$

Complex	k x 10^4,sec^{-1} (Temp.,°C)	E_a-I (kcal/mol)	E_a-II (kcal/mol)
$[Ru(H_2O)(NH_3)_5]Br_3$	0.768 (40) 1.73 (49) 2.88 (54) 6.65 (58) 47.0 (80)[a]	26.8	23.0
$[Ru(H_2O)(NH_3)_5](NO_3)_3$	2.38 (41) 5.07 (49) 7.53 (55) 17.96 (63) 72.5 (80)[a]	19.0	17.5
$[Co(H_2O)(NH_3)_5]Br_3$[b]	4.79 (85) 7.59 (90) 11.5 (93.7)		25 ± 2
$[Co(H_2O)(NH_3)_5](NO_3)_3$[b]	1.70 (82) 2.51 (85) 3.55 (88)		31 ± 3
$[Cr(H_2O)(NH_3)_5]Br_3$		38[c]	36[c], 31[d]
$[Cr(H_2O)(NH_3)_5](NO_3)_3$		18[c]	14[c], 16[d]

a) Extrapolated values. b) From Ref.3. c) From Ref.6. d) From Ref.5.

for the corresponding complex nitrates, while this relation is not observed for the cobalt(III) compounds. The reason for this may be attributed to the presence of a low-lying unoccupied d-orbital for chromium(III), t_{2g}^3 and ruthenium(III), t_{2g}^5 metal ions, but a more decisive reason is not clear.

Considering the mechanism of deaquation-anation, it is convenient to divide the reaction (1) into the two kinds of reaction schemes (2)→(3), or (4)→(5).

$[Ru(H_2O)(NH_3)_5]X_3 \rightarrow [Ru(NH_3)_5]X_3 + H_2O$ (2), $[Ru(NH_3)_5]X_3 \rightarrow [RuX(NH_3)_5]X_2$ (3) and

$[Ru(H_2O)(NH_3)_5]X_3 \rightarrow [RuX(H_2O)(NH_3)_5]X_2$ (4), $[RuX(H_2O)(NH_3)_5]X_2 \rightarrow [RuX(NH_3)_5]X_2 + H_2O$ (5).

If the reaction path(2) is the rate-determining step, the activation energies in the two kinds of compounds should be approximately close to each other. When the rate of the anation process(4) is smaller than that if the deaquation process(2), the deaquation-anation reaction will belong to the S_N2 mechanism. The experimental results as shown in Table 1 support the latter reaction mechanism. When the addition of the nucleophile is reversible and the rate-determining step is the loss of the leaving group, this can be said the S_N2 mechanism[9] since both bond making and bond breaking simultaneously occur. In this case, the rates would show the characteristic behavior of displacement mechanisms in that the nature of the entering group would exert a significant effect on the rates of the reaction. As is shown in Table 1, the rate constants for the nitrates are nearly three-fold larger than those for the bromides and the activation energy for the latter is about 1.4-fold larger than that for the former compound. This may suggest that the deaquation-anation reaction will take place through the reactions (4) and (5), that is S_N2 mechanism. These relations are in agreement with that predicted from the crystal-field activation energy[10] assuming a seven-coordinated intermediate in the reaction corresponding to the reaction (4). Moreover, the reaction in the solid state will be more favorable to take the S_N2 mechanism different from that in the aqueous phase, because the outer-sphere anion may be fixed by the lattice energy at the neighboring position to the inner-sphere ligand in solid state.

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