BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(4), 841—846 (1974)

Thermal Decomposition Reaction of Halogenoammineruthenium(III) Halide Complexes[1)]

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(Received April 17, 1973)

The thermal decomposition of halogenopentaammine- and *cis*-dihalogenotetraammineruthenium(III) complexes was studied by the techniques of thermogravimetry(TG), differential thermal analysis(DTA), and evolved gas analysis(EGA). The stoichiometry of the decomposition reaction was determined by the analysis of the reaction intermediates and products. The order of decreasing thermal stability, as well as order of temperature of mass-loss initiation, seems to be: $[RuCl(NH_3)_5]Cl_2 > [RuBr(NH_3)_5]Br_2 > [RuI(NH_3)_5]I_2$ for monohalogeno complexes, and *cis*-$[RuCl_2(NH_3)_4]Cl >$ *cis*-$[RuBr_2(NH_3)_4]Br >$ *cis*-$[RuI_2(NH_3)_4]I$ for dihalogeno complexes. Trihalogenotriammine complexes were observed as intermediates for the cases of dichloro and bromo complexes. a simple decomposition reaction was found for the iodo complexes, and then the activation energy for the following reaction was determined: $[RuI(NH_3)_5]I_2 \rightarrow RuI_3 + 5NH_3$, $E_a = 41.9$ kcal/mol and *cis*-$[RuI_2(NH_3)_4]I \rightarrow RuI_3 + 4NH_3$, $E_a = 27.8$ kcal/mol. The reaction mechanisms may be summarized as follows: (a) an electron-transfer mechanism, in which the ruthenium(III) was reduced by the ammonia molecule or the halide ion, (b) the thermal splitting of the ruthenium-ammine bond, and (c) the bond formation between the ruthenium(III) and the halide ion after the ion migration from the outersphere to the innersphere of the complex. The predominant factors which control these mechanisms may be the coordinate bond strength of the ruthenium(III) and various ligand species, the relative potential of electron transfer from the ligand to the ruthenium(III), and the ease of halide-ion migration from the outersphere to the innersphere of the complex.

The thermal decomposition of a number of cobalt(III)[2—9)] and chromium(III)[10—15)] ammine complexes has been previously reported. Recently, the thermal decomposition of hexaammineruthenium(III) chloride only has been studied by Trehoux *et al.*[16)] It is thus the object of this investigation to study the thermal decomposition of complexes of the $[RuX(NH_3)_5]X_2$ and $[RuX_2(NH_3)_4]X$ type, where X is Cl^-, Br^-, and I^-, by the techniques of thermogravimetry(TG), differential thermal analysis(DTA), and evolved gas analysis(EGA). The reaction intermediates and products were analyzed by spectrophotometry.

Experimental

Preparation of Ruthenium Complexes. $[RuCl(NH_3)_5]Cl_2$, $[RuBr(NH_3)_5]Br_2$, and $[RuI(NH_3)_5]I_2$ were prepared from ruthenium trichloride, hydrazine hydrate, and the respective hydrohalogenic acid by the method of Allen and Senoff.[17)] The $[RuX_2(NH_3)_4]X$, ($X = Cl^-$, Br^- and I^-) were prepared by the method of Gleu and Breuel.[18)] The compounds thus prepared were analyzed by the usual elemental analysis and confirmed by studying their electronic spectra.

Apparatus and Procedure. A Shimadzu D. T. 20B micro-differential thermal analyzer connected with an EGD 20 evolved gas detector was used for a series of thermal-decomposition reactions. Another series of experiments formed the thermogravimetry of a complex by using a Shimadzu T.G.C. 20-type microthermobalance. A Shimadzu UV 200 recording spectrophotometer was used for the measurement of the absorption spectra of the initial complexes, reaction intermediates, and products.

Samples of about 5—8 mg were pyrolyzed in a dynamic helium atmosphere in a furnace at a heating rate of 5 °C per min. The electric responses corresponding to the variation in the temperature, the gas evolution, and the sample massloss were recorded as functions of the furnace temperature on a potentiometric recorder with a sensitivity of ± 50 μV.

The reaction products were analyzed as follows. The sample of about 30—40 mg was pyrolyzed in dynamic helium by using a differential thermal analyzer connected with a gas evolution detector. The liberated ammonia gas was absorbed in a series of traps containing 0.02 M sulfuric acid. For all the aliquots of the trap solution, the concentration of ammonia was determined by potentiometric titration with a 0.02 M sodium hydroxide standard solution. An aliquot of the solution was also used for the colorimetric determination of ammonia with the Nessler reagent.

The liberated halogen gas was dissolved in a dilute potassium iodide solution and titrated with a standard sodium thiosulfate solution.

The reaction products, which were condensed on the wall of apparatus, were collected and identified by the tests for ammonium ion and halide ions. The final reaction product was analyzed by direct weighing and found to be ruthenium oxide after heating in the air. To analyze the halide content, titration with the potassium thiocyanate standard solution was carried out after dissolving the product in water and adding an excess of a standard silver nitrate solution.

The UV and visible spectra were measured in order to identify some decomposition intermediates and products.

Results and Discussion

Differential Thermal Analysis-Gas Evolution Studies. The DTA and GE curves of the monohalogenopenta-amineruthenium(III) and *cis*-dihalogenotetraammineruthenium(III) halogenides are given in Figs. 1 and 2. All of the DTA curves of the monohalogenopenta-ammineruthenium(III) halogenides are characterized by an endothermic peak: at 313 °C (chloro complex), 319 °C (bromo complex), and 258 °C (iodo complex) respectively. A small peak was also observed at 388 °C for the last complex. Each endothermic peak corresponds well to the respective peak on the GE curves. This fact shows that the main decomposition reaction, probably taking place during the first endothermic reaction, is accompanied by the evolution of such gases as ammonia, free halogen and/or ammonium halide. The DTA curves of the *cis*-dihalogenotetra-

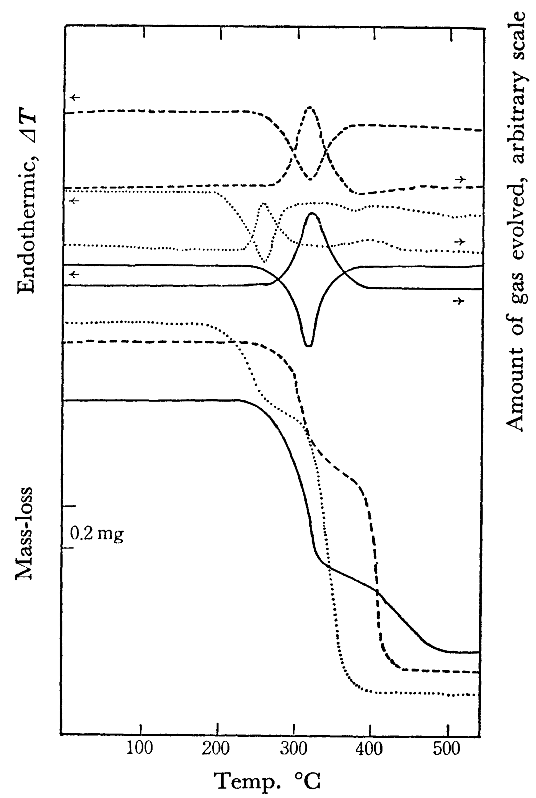

Fig. 1. DTA, GE and TG curves of $[RuX(NH_3)_5]X_2$, in a helium atmosphere. —— X=Cl, ---- X=Br, ······ X=I.

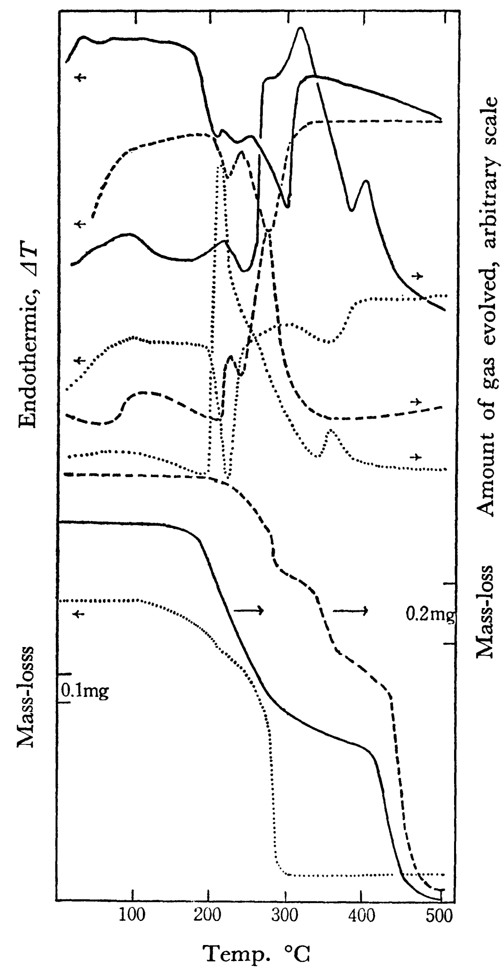

Fig. 2. DTA, GE and TG curves of $[RuX_2(NH_3)_4]X$, in a helium atmosphere. —— X=Cl, ---- X=Br, ······ X=I.

ammineruthenium(III) halogenides (Fig. 2) are different from each other and also from those of the monohalogeno complexes. In particular, that of the dichloro complex shows an endothermic peak at 246 °C between the first (220 °C) and the third (310 °C) peaks. For both the dibromo and the diiodo complex, the DTA curves show two endothermic peaks; however, the relative intensities of the first to the second peak is different. For the dichloro and dibromo complexes, the last peak is the largest, while for the diiodo complex, first peak at 220 °C is sharper and larger than the last one (353 °C). The temperature at each peak on the GE curves in Fig. 2 corresponds to that at the respective endothermic peak on the DTA curves. From this fact, it may be concluded that all the decomposition reactions are endothermic and gas-evolving.

Thermogravimetric Analysis. The curves obtained by the thermogravimetry(TG) are given in Figs. 1 and 2. The thermal decomposition is initiated at 246 °C (chloro complex), 244 °C (bromo complex), 174 °C (iodo complex), 200 °C (dichloro complex), 210 °C (dibromo complex), and 114 °C (diiodo complex). The initial decomposition temperature of each dihalogeno complex is generally lower than that of the corresponding monohalogeno complex, while the final temperature for the mass-loss is higher than that of the monohalogeno complex, except in the case of the iodo complex.

The orders of the decrease in thermal stability, along with the temperature of mass-loss initiation, seem to be: $[RuCl(NH_3)_5]Cl_2 > [RuBr(NH_3)_5]Br_2 > [RuI(NH_3)_5]I_2$ for the monohalogeno complexes and *cis*-$[RuCl_2(NH_3)_4]Cl >$ *cis*-$[RuBr_2(NH_3)_4]Br >$ *cis*-$[RuI_2(NH_3)_4]I$ for the dihalogeno complexes. The complexes containing iodide were certainly least stable. Similar relations have been reported in the thermal decomposition studies of halogenoammine complexes of cobalt(III)[3,5,7] and chromium(III).[13]

Table 1 shows the numerical data of mass-loss studies along with those of evolved gas analysis. The calculated mass-loss values for chloro complexes could not be determined because of their continuous thermal decompositions. From these results, the intermediate products were estimated to be as follows: $RuBr_2$ at 398 °C for the monobromo complex and at 431 °C for the dibromo complex; RuI_3 at 268 °C for the monoiodo complex and at 222 °C for the diiodo complex.

Product-analysis Studies. Table 2 shows the results of the evolved-ammonia-gas analyses, the mass of the final reaction products, and the molar ratios of ammonia to ruthenium metal. The mass of the final product is nearly in agreement with that of the ruthenium metal in each complex. The molar ratios (NH_3/Ru) are different from each other, however all the ammine ligands in the iodo complexes are liberated as ammonia molecules, while only three molecules for bromo complexes and only one or two for chloro complexes are liberated. These facts suggest that the

TABLE 1. MASS-LOSS DATA FOR HALOGENOAMMINERUTHENIUM(III) COMPLEXES

Complex		Mass-loss (%)		
$[RuCl(NH_3)_5]\cdot Cl_2$	Temp. (°C)	246—396	396—466	
	Experimental	47.0	16.0	
	Theoretical	—	—	
	Evolved gas	NH_3, NH_4Cl, HCl	HCl, Cl_2	
$[RuBr(NH_3)_5]\cdot Br_2$	Temp. (°C)	244—398	398—440	
	Experimental	35.8	39.3	
	Theoretical	38.7	37.5	
	Evolved gas	NH_3, NH_4Br	Br_2	
$[RuI(NH_3)_5)_5]I_2$	Temp. (°C)	136—268	268—476	
	Experimental	16.5	65.2	
	Theoretical	15.0	67.2	
	Evolved gas	NH_3	I_2	
$[RuCl_2(NH_3)_4]\cdot Cl\cdot 2/5H_2O$	Temp. (°C)	63—200	200—419	419—521
	Experimental	2.6	37.2	25.1
	Theoretical	—	—	—
	Evolved gas	H_2O	HH_3, NH_4Cl, HCl	HCl, Cl_2
$[RuBr_2(NH_3)_4]\cdot Br$	Temp. (°C)		210—431	431—473
	Experimental		37.7	37.4
	Theoretical		36.9	39.1
	Evolved gas		NH_3, NH_4Br	Br_2
$[RuI_2(NH_3)_4]\cdot I$	Temp. (°C)		114—222	222—320
	Experimental		13.3	68.3
	Theoretical		12.4	69.2
	Evolved gas		NH_3	I_2

TABLE 2. DETERMINATION OF EVOLVED AMMONIA GAS AND RESIDUE

Complex	Sample weight (mol)	NH_3 Calcd	Residue (%) Obsd	Ru (%) Calcd	Molar ratio, NH_3/Ru
$[RuCl(NH_3)_5]Cl_2$	8.60×10^{-5}	1.93×10^{-4}	35.0	34.6	2.2
$[RuBr(NH_3)_5]Br_2$	9.65×10^{-5}	3.25×10^{-4}	24.8	23.7	3.4
$[RuI(NH_3)_5]I_2$	5.43×10^{-5}	2.65×10^{-4}	17.4	17.8	4.9
cis-$[RuCl_2(NH_3)_4]Cl2/5H_2O$	1.14×10^{-4}	1.52×10^{-4}	35.9	36.7	1.3
cis-$[RuBr_2(NH_3)_4]Br$	9.56×10^{-5}	2.59×10^{-4}	25.6	24.7	2.7
cis-$[RuI_2(NH_3)_4]I$	6.35×10^{-5}	2.70×10^{-4}	20.0	18.4	4.1

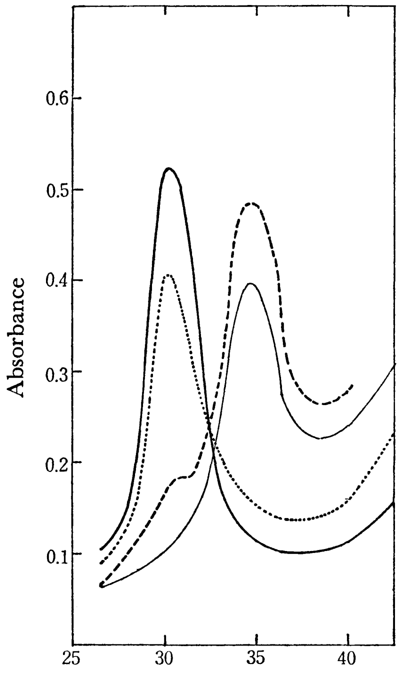

Fig. 3. Absorption spectra of thermal decomposition products for $[RuCl(NH_3)_5]Cl_2$. —— room temp., ······ 260 °C, ---- 297 °C, —— 396 °C.

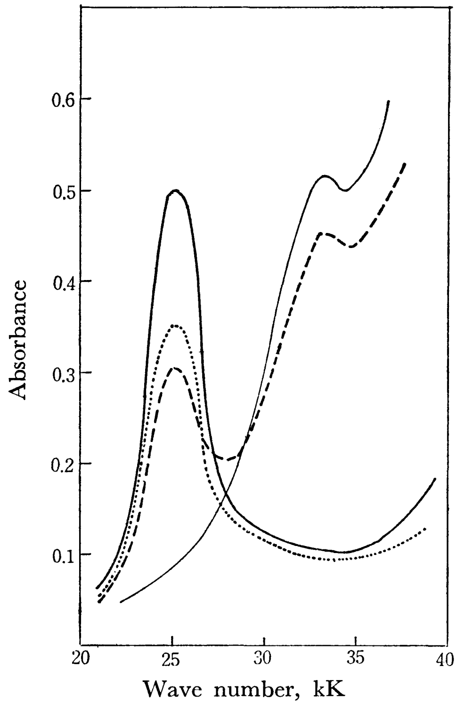

Fig. 4. Absorption spectra of thermal decomposition products for $[RuBr(NH_3)_5]Br_2$. —— room temp., ······ 265 °C, ---- 300 °C, —— 320 °C.

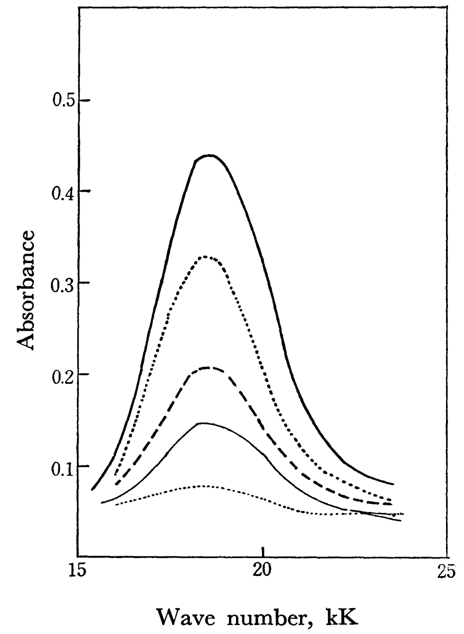

Fig. 5. Absorption spectra of thermal decomposition products for $[RuI(NH_3)_5]I_2$ —— room temp., ···· 203 °C, ---- 210 °C, —— 230 °C, ······ 240 °C.

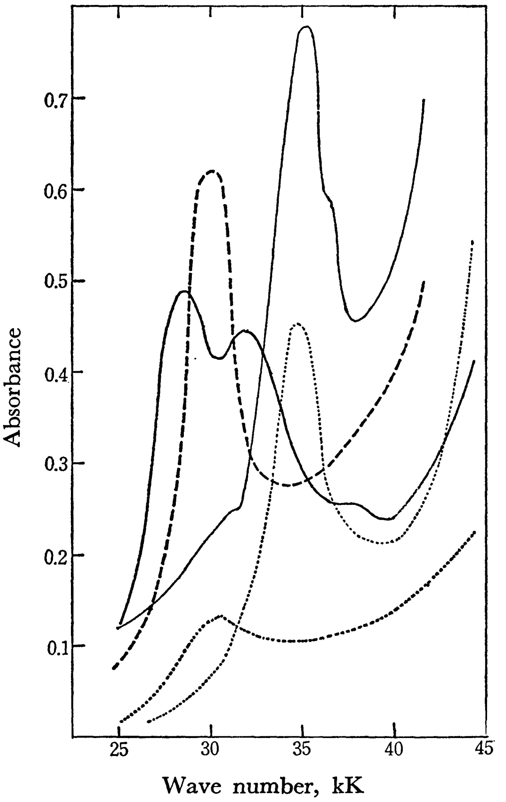

Fig. 6. Absorption spectra of thermal decomposition products for *cis*-$[RuCl_2(NH_3)_4]Cl$. —— room temp., ···· 215 °C, ---- 235 °C, —— 300 °C, ······ 419 °C.

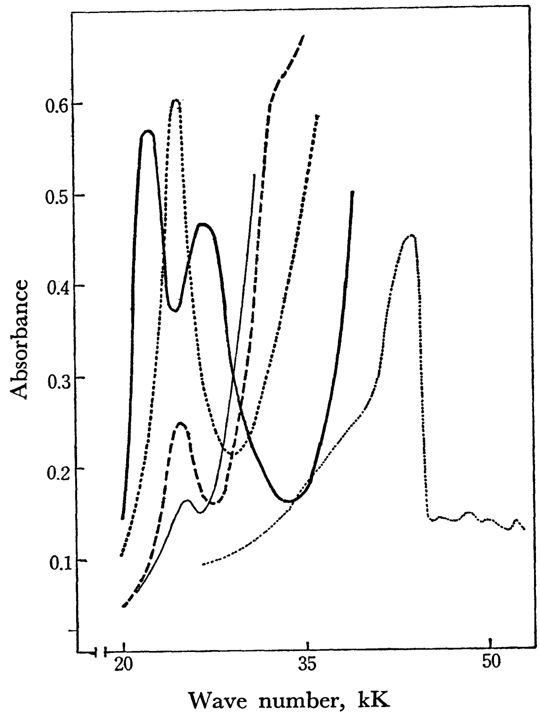

Fig. 7. Absorption spectra of thermal decomposition products for *cis*-$[RuBr_2(NH_3)_4]Br$. —— room temp., ···· 215 °C, ---- 240, 260 °C, —— 280 °C, ······ 416 °C.

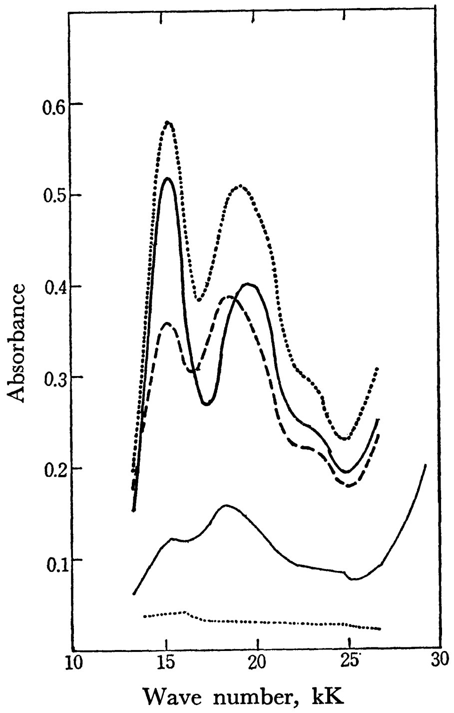

Fig. 8. Absorption spectra of thermal decomposition products for *cis*-$[RuI_2(NH_3)_4]I$. —— room temp., ···· 150 °C, ---- 180 °C, —— 200 °C, ······ 230 °C.

contribution of the halide ion to the weakening of the strength of the ruthenium–ammine coordinate bond is variable.

The absorption spectra of the initial complexes and the decomposition intermediates are shown in Figs. 3—8. The temperature for the sampling of the intermediates was selected by reference to the variation points on the DTA and TG curves. The initial spectrum of the monochloro complex shows an absorption peak at 30.5 kK which decreases with the progress of the thermal decomposition, and a new peak appears at 34.7 kK. The formation of trichlorotriammine complex was apparently confirmed by the appearance of a peak at 30.2 kK in the spectra of the intermediates obtained at 215 and 235 °C only in the case of the dichloro complex, as is shown in Fig. 6, while it was difficult to identify this complex in the case of the monochloro complex. A similar complex has been assumed to be the same as an intermediate in the thermal decomposition of the hexaammineruthenium(III) trichloride by Trehoux *et al.*[16] The absorption peak at 34.7 kK in the spectra of the final products in Figs. 3 and 6 has not yet been assigned definitely. The chemical formula of this product was estimated to be Ru_2Cl_2-NH_3 from the results of elemental analysis. These facts suggest that the ruthenium(III) has already been reduced to the low valence state when the temperature is elevated to 297 °C.

As is shown in Fig. 4, the absorption peak at 25.1 kK ascribed to the monobromo complex decreases with a slight shift toward the side of higher wave numbers. A new peak at 33.1 kK begins to appear in the spectrum of the intermediate obtained at 300 °C (Fig. 4). In the spectrum of the intermediate obtained at 320 °C, the 25.1 kK peak has entirely disappeared, and the spectrum is found to consist of 33.1 kK peak and a continuous absorption in the region of ultraviolet wavelengths (Fig. 4). This 33.1 kK peak has not yet been assigned. The variations in the absorption spectra in the course of thermal decomposition for *cis*-dibromotetraammine appear to be somewhat complex. The character of the spectrum of the initial complex has entirely vanished in that of the intermediate obtained at 215 °C (Fig. 7). At this temperature, the deammonation has already started, as is shown by the endothermic peak at 226 °C and the mass-loss curve starting at 210 °C in Fig. 2. The absorption peak at 24.9 kK in the spectrum of the intermediate obtained at 215 °C may be attributable to the tribromotriammine complex because the spectral change is similar to that corresponding to the transformation from *cis*-dichlorotetraammine to the trichlorotriammineruthenium(III) complex.

The absorption spectra of intermediates produced in both the thermal decompositions of iodopentaammine and *cis*-diiodotetraammineruthenium(III) iodides show the continuous variation, as is shown in Figs. 5 and 8. Such a variation in the spectrum suggests that only deammonation is continuously proceeding because of the difficulty of the substitution reaction by the iodide ions in the outerspheres of complexes.

Stoichiometry of the Thermal-decomposition Reaction. In view of the results obtained from the DTA, EGA, and TG and the product analysis, the following thermal decomposition reactions are presumably established. For the chloroammineruthenium(IIII) complexes:

$$[RuCl(NH_3)_5]Cl_2 \rightarrow [RuCl_3(NH_3)_3] + 2NH_3 \tag{1}$$

$$\rightarrow Ru + 2NH_3 + 2NH_4Cl + HCl + 1/2\,N_2 \tag{2}$$

$$[RuCl_2(NH_3)_4]Cl \rightarrow [RuCl_3(NH_3)_3] + NH_3 \tag{3}$$

$$\rightarrow Ru + NH_3 + 2NH_4Cl + HCl + 1/2\,N_2 \tag{4}$$

For the bromoammineruthenium(III) complexes:

$$2[RuBr(NH_3)_5]Br_2 \rightarrow 2[RuBr_3(NH_3)_3] + 4NH_3 \tag{5}$$

$$\rightarrow 2RuBr_2 + 7NH_3 + 2NH_4Br + 1/2\,N_2 + 1/2\,H_2 \tag{6}$$

$$\rightarrow 2Ru + 2Br_2 + 7NH_3 + 2NH_4Br + 1/2\,N_2 + 1/2\,H_2 \tag{7}$$

$$2[RuBr_2(NH_3)_4]Br \rightarrow 2[RuBr_3(NH_3)_3] + 2NH_3 \tag{8}$$

$$\rightarrow 2RuBr_2 + 5NH_3 + 2NH_4Br + 1/2\,N_2 + 1/2\,H_2 \tag{9}$$

$$\rightarrow 2Ru + 2Br_2 + 5NH_3 + 2NH_4Br + 1/2\,N_2 + 1/2\,H_2 \tag{10}$$

For the iodoammineruthenium(III) complexes:

$$[RuI(NH_3)_5]I_2 \rightarrow RuI_3 + 5\,NH_3 \tag{11}$$

$$\rightarrow Ru + 3/2\,I_2 + 5\,NH_3 \tag{12}$$

$$[RuI_2(NH_3)_4]I \rightarrow RuI_3 + 4\,NH_3 \tag{13}$$

$$\rightarrow Ru + 3/2\,I_2 + 4\,NH_3 \tag{14}$$

The intermediates of the above reactions, the trichlorotriammineruthenium(III), $[RuCl_3(NH_3)_3]$, and the ruthenium dibromide, $RuBr_2$, were confirmed by the elemental analysis.

Found: H, 3.60; N, 16.52%. Calcd for $[RuCl_3$-$(NH_3)_3]$: H, 3.48, N, 16.24%.

Found: Br, 61.6%. Calcd for $RuBr_2$: Br, 62.2%.

From the above reaction scheme, we have noted that the complexes are dissociated by two different mechanisms, that is, that in which the ruthenium(III) is reduced by the halide ion and that in which the ruthenium(III) is reduced by the ammonia molecule. Of course, the displacement of ligand species by the halide ions in the outersphere of the complex was also observed.

One of the probable factors controlling the two different mechanisms may be the relative reducing power of the ligands, which is presumed, from the order of their reduction potentials, to be $I^- > Br^- > NH_3 > Cl^-$. By this assumption, it can be interpreted that the ruthenium(III) is reduced by the ammonia molecule in the thermal-decomposition reactions of chloro- and bromopentaammine complexes, while the ruthenium(III) is reduced by iodide in the iodopentaammine complex.

The monohalogenopentaammine complexes are thermochemically more stable than the corresponding dihalogeno complexes, while the iodo complexes are the least stable of the series of complexes. This means that the bond nature of the ruthenium(III)-ammine ligand may be reflected by the bond strength of the ruthenium(III)-halogen ligand.

The order of the thermal stability, chloro complexes> bromo complex>iodo complex, is also in agreement with that of the strength of the ruthenium(III)-ammine bond as estimated from the vibrational frequencies of the complexe, *i. e.*, the ν(Ru–N) values are 485, 463 and 451 cm^{-1} for chloropentaammines>479, 459 and 448 cm^{-1} for bromopentaammine>468, 450, 442 and 424 cm^{-1} for iodopentaammine, as has been re-

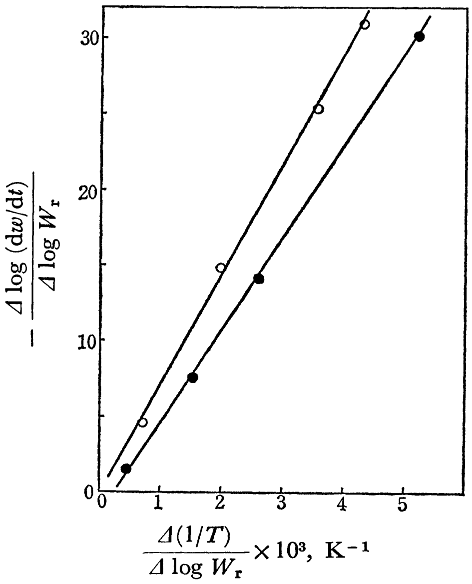

Fig. 9. The plots of Freeman-Carroll equation for the reaction, $[\mathrm{RuI}_n(\mathrm{NH_3})_{6-n}]\mathrm{I}_{3-n} \rightarrow (6-n)\mathrm{NH_3} + 3/2\,\mathrm{I_2}$, $n=1$ and 2. $W_r = w_0 - w$, w_0 = weight loss at completion of reaction, w = total weight loss up to time t. ○ diiodo complex, ● monoiodo complex

ported by Allen and Senoff.[17]

The Thermal-reaction Kinetics. Since the decompositions of iodo complexes were definitely observed to consist of ammonia-gas and free-iodine liberations, the kinetic treatment of the ammonia-gas evolution reaction for two iodo complexes was made using the method of Freeman and Carroll.[19] These kinetic plots are shown in Fig. 9; the activation energies were calculated as follows:

$[\mathrm{RuI(NH_3)_5}]\mathrm{I_2} \rightarrow 5\mathrm{NH_3} + \mathrm{RuI_3}$, 41.7 ± 0.7 kcal/mol

$[\mathrm{RuI_2(NH_3)_4}]\mathrm{I} \rightarrow 4\mathrm{NH_3} + \mathrm{RuI_3}$, 27.8 ± 0.2 kcal/mol

Wendlandt and Smith[4] reported the activation energy for the deammonia reaction of halogenopentaamminecobalt(III) to be 28 kcal/mol for chloropentaammine and 21 kcal/mol for bromopentaammine. Though the species of the halide ligands are different, these values are smaller than that of iodopentaammineruthenium(III). This fact may suggest that the metal-ammine bond is stronger in the ruthenium(III) complex than in the cabalt(III) complex, because the metal-halide bond strength is rather the reverse.

The authors wish to thank the Ministry of Education for the financial support granted to this research.

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