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THERMAL DECOMPOSITION REACTION OF HALOGENOPENTAAMMINERUTHENIUM(III) COMPLEXES

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The thermal decomposition reaction of halogenopentaammineruthenium (III) complexes was studied by the techniques of thermogravimetry, differential thermal analysis and evolved gas analysis. The complexes were dissociated by two different mechanisms: (a) those in which the Ru(III) was reduced by halide ion; and (b) those in which the Ru(III) was reduced by ammonia molecule. Which mechanism is preferably selected for a thermal decomposition reaction, it seems to be determined by the composition of ligands in the complexes.

Although there have been many studies on the thermal decomposition reactions of cobalt(III) and chromium(III) complexes, similar reactions of ruthenium(III) complexes have scarcely been studied. Recently, Trehoux and co-workers[1] reported that hexaammine ruthenium(III) chloride was decomposed in inert gas to metallic ruthenium through the intermediates, $[RuCl(NH_3)_5]Cl_2$, $[RuCl_2(NH_3)_4]Cl$ and $[RuCl_3(NH_3)_3]$ between 200 and 400°C.

It is thus the object of this investigation to study the thermal decompositions of complexes, $[RuX(NH_3)_5]X_2$, where X is Cl^-, Br^- and I^-. The reactions were studied by the thermogravimetry(TG), differential thermal analysis(DTA) and evolved gas analysis(EGA) and the stoichiometry was also determined by analysis of the reaction intermediates and products.

Halogenopentaammineruthenium(III) halides were prepared from ruthenium trichloride, hydrazine hydrate and respective hydrohalogenic acid by the method of Allen and Senoff.[2] These compounds prepared were analysed by the usual elemental analysis and confirmed by the electronic spectra.

A Shimadzu D.T.20B micro-differential thermal analyzer connected with EGD 20 evolved gas detector was used for a series of thermal decomposition reactions. Another series of experiments was the thermogravimetry of complexes using a Shimadzu T.G.C. 20 type micro-thermobalance. A Shimadzu UV 200 recording spectrophotometer was used for measurements of absorption spectra of initial complexes, reaction intermediates and final products. About 5 mg of samples were pyrolyzed in a dynamic helium atmosphere in a furnace with a heating rate of 5°C per min. The electric responses corresponding to the temperature variation, gas evolution and the mass loss were recorded as a function of the temperature on a potentiometric recorder. The ammonia gas liberated was absorbed in a series of traps containing 0.02 M sulfuric acid. The concentration of ammonia was determined by the potentiometric titration with a 0.02 M sodium hydroxide standard solution and by the colorimetry with the Nessler reagent. The reaction intermediate, which was condensed on the wall of apparatus was collected and identified by tests for ammonium ion and halide ions. The final reaction product was analysed by the direct

weighing as ruthenium oxide after a 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 standard silver nitrate solution. U.V. and visible spectra were measured to identify some reaction intermediates.

The DTA and EGA curves of halogenopentaammineruthenium(III) halogenides are given in Fig.1. Each of the DTA curves was characterized by an endothermic peak at 313°C (chloro complex), 319°C (bromo complex) and 258°C (iodo complex), respectively. The peak of the last complex was also followed by a small peak at 388°C. Each endothermic peak is well corresponding to the respective peak of EGA curves. This fact shows that the main decomposition reaction probably taking place during the first endothermic peak is followed by the evolution of gases such as free halogen, ammonia and/or ammonium halide.

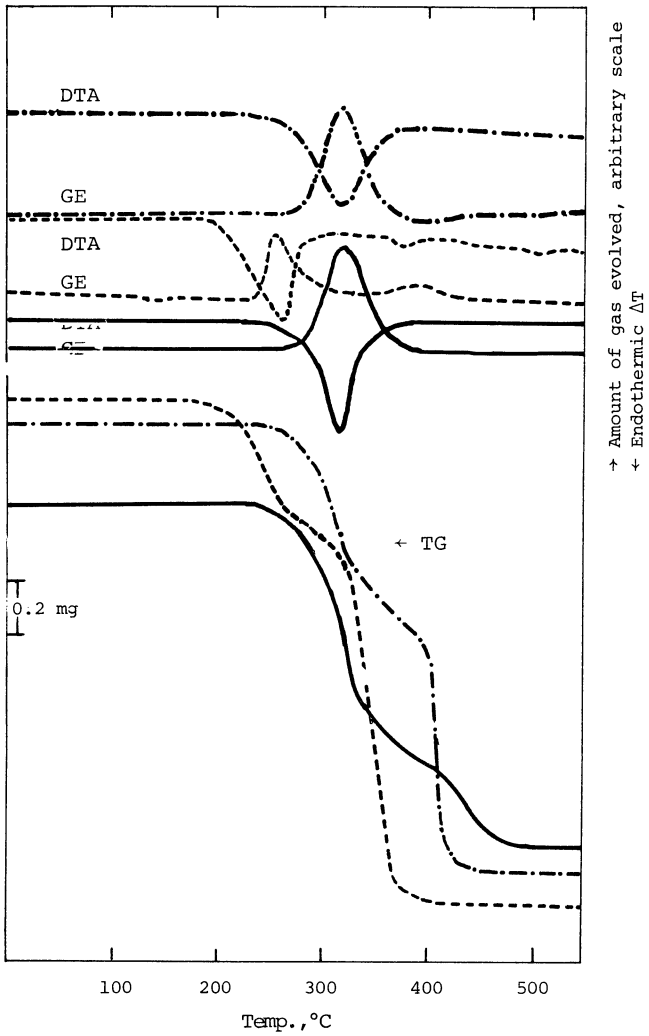


Fig.1. DTA,GE, and TG curves of $[RuX(NH_3)_5X_2$
— $[RuCl(NH_3)_5]Cl_2$, -·- $[RuBr(NH_3)_5]Br_2$, ···· $[RuI(NH_3)_5]I_2$.

The curves obtained by the thermogravimetry (TG) are also given in Fig.1. The thermal decomposition is respectively initiated at 246°C (chloro complex), 244°C (bromo complex), and 174°C (iodo complex). The order of decreasing of thermal stability, along with the temperature of mass-loss initiation was: $[RuCl(NH_3)_5]Cl_2$ > $[RuBr(NH_3)_5]Br_2$ > $[RuI(NH_3)_5]I_2$. The complex containing iodide was certainly least stable. Similar relations have been reported in the thermal decomposition studies of halogenoammine complexes of cobalt(III)[3-5] and chromium(III).[6]

Table 1 shows the numerical data of mass-loss studies along with those of evolved gas analysis. The calculated mass-loss values for the chloro complex could not be determined due to their continuous thermal decomposition. These results show that the intermediate products were probably as follows: $RuBr_2$ at 398°C for bromo complex; RuI_3 (or $[RuI_2]I$) at 268°C for iodo complex.

Table 2 shows the results of the evolved ammonia gas analysis, the weight percentages of the final reaction residues and the molar ratios of ammonia to ruthenium metal. The weight of residue is nearly in agreement with that of the ruthenium metal in each complex. This fact shows that the final decomposition product is the metallic ruthenium alone. All the ammine ligands in the iodo complex are liberated as ammonia

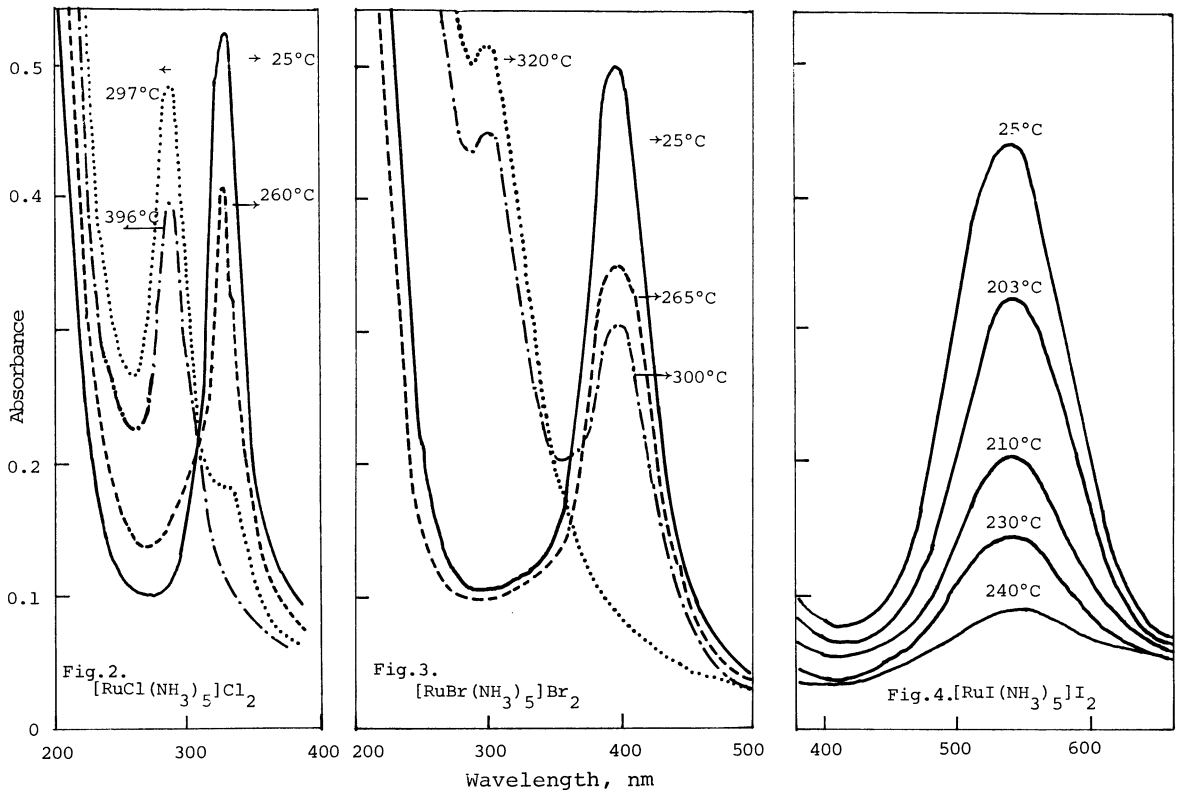
molecules, while 3.4 molecules for bromo complex and 2.2 molecules for chloro complex are only liberated. This may suggest some contribution of the halide ion to weaken the strength of ruthenium-ammine coordinate bond.

Table 1. Mass loss data for halogenopentaammineruthenium(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
$[RuI(NH_3)_5]I_2$	temp(°C)	136 - 268	268 - 476
	experimental	16.5	65.2
	theoretical	15.0	67.2
	evolved gas	NH_3	I_2

Table 2. Determination of evolved ammonia gas and residue.

complex	Sample weight, 10^{-5}M	NH_3, 10^{-4}M calcd.	Residue(%) obs.	Ru(%) calcd	molar ratio NH_3/Ru
$[RuCl(NH_3)_5]Cl_2$	8.60	1.93	35.0	34.6	2.2
$[RuBr(NH_3)_5]Br_2$	9.65	3.25	24.8	23.7	3.4
$[RuI(NH_3)_5]I_2$	5.43	2.65	17.4	17.8	4.9



Absorption spectra of the initial complexes and the reaction intermediates are shown in Figs.2,3 and 4. The temperature for the sampling of the intermediates was selected referring to the variation points on the DTA and TG curves. The initial spectrum of chloro complex shows an absorption maximum at 328 nm. This peak decreases with the proceeding of the thermal decomposition, while a new peak appears at 285 nm. Both the spectra of intermediates at 260 and 297°C show the shoulder at 334 nm. This change of spectrum may be attributable to the formation of trans-dichlorotetraammine whose ν_{max} is known at 334 nm. A peak at 285 nm in the spectrum of the final product could not be assigned, but the results of elemental analysis showed the composition to $Ru_2Cl_2NH_3$. The trichlorotriammineruthenium(III) complex has been assumed as an intermediate in the thermal decomposition of the hexaammineruthenium(III) trichloride.[1] In our experiment, the 331 nm peak of this intermediate could not be apparently confirmed due to the 334 nm peak of trans-dichlorotetraammine complex. As is shown in Fig.3, an absorption peak at 399 nm ascribed to the bromo complex decreases with a slight shift to the shorter side of wavelength. A new peak at 302 nm begins to appear in the spectrum of intermediate obtained at 300°C. In the spectrum of intermediate obtained at 320°C, the 399 nm peak has entirely disappeared, and the spectrum was found to consist of 302 nm peak and the continuous absorption in the region of ultraviolet wavelength. Absorption spectra of intermediates in the thermal decomposition of iodopentaammine show the continuous variations as illustrated in Fig.4. Such variation of the spectrum suggests that only deammonation is continuously proceeding due to the difficulty of the substitution reaction by the iodide ions in the outer-sphere of complex.

From the results obtained from the DTA,EGA and TG studies and the product analysis, the following thermal decomposition reactions seem to occur.

$$[RuCl(NH_3)_5]Cl_2 \rightarrow [RuCl_3(NH_3)_3] + 2NH_3 \rightarrow Ru + 2NH_3 + 2NH_4Cl + HCl + 1/2\ N_2 \quad (1)$$

$$2[RuBr(NH_3)_5]Br_2 \rightarrow 2[RuBr_3(NH_3)_3] + 4NH_3 \rightarrow 2RuBr_2 + 7NH_3 + 2NH_4Br + 1/2\ N_2 + 1/2\ H_2 \rightarrow 2Ru + 2Br_2 + 7NH_3 + 2NH_4Br + 1/2\ N_2 + 1/2\ H_2 \quad (2)$$

$$[RuI(NH_3)_5]I_2 \rightarrow RuI_3\ (\text{or}\ [RuI_2]I) + 5NH_3 \rightarrow Ru + 3/2\ I_2 + 5NH_3 \quad (3).$$

From the above reaction scheme, it may be concluded that the complexes are decomposed by different mechanisms, that is, those in which the ruthenium(III) is reduced by halide ion and those in which the ruthenium(III) is reduced by ammonia molecule. The deammonation and the ligand migration are also contained in the reactions. One of the factors controlling the mechanism may be the bond strength of ruthenium-ammine or halide ligand which can be estimated from the vibrational frequencies.[2] The other one may be the relative reducing power of ligands which can be presumed from the order of their reduction potentials to be $I^- > Br^- > NH_3 > Cl^-$. By these assumptions, it can be interpreted that the order of the thermal stability is chloro complex > bromo complex > iodo complex.

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