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Studies of Ruthenium Complexes. VIII.[1] Kinetic Studies of the Thermal Substitution Reaction of Hexaammine and *cis*-Dihalogenotetraammineruthenium(III) Complexes in the Solid State

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The Kinetics of the thermal substitution reaction of hexaammineruthenium(III) halides and *cis*-dihalogenotetraammineruthenium(III) halides have been studied in the solid state. The reaction rates and kinetic parameters were determined for these two reactions; $[Ru(NH_3)_6]X_3 \rightarrow [RuX(NH_3)_5]X_2 + NH_3$, (X=Br, I) and *cis*-$[RuX_2(NH_3)_4]X \rightarrow [RuX_3(NH_3)_3] + NH_3$, (X=Cl, Br). The values of the rate constant, the activation energy, and the activation entropy were $2.10 \times 10^{-5}\ s^{-1}$ (at 161 °C), 23.3 kcal mol^{-1}, and −29.3 e.u. for the hexaammine bromide, and $2.92 \times 10^{-5}\ s^{-1}$ (at 162 °C), 31.3 kcal mol^{-1}, and −10.1 e.u. for the *cis*-dibromotetraammine bromide. The S_N2 mechanism is more probable for the former reaction, while the S_N1 mechanism is more probable for the latter reaction.

It has previously been reported that the thermal-decomposition reaction of a chromium(III) complex having volatile ligands such as ammonia, water, and ethylenediammine is initiated by the replacement of a ligand by an outersphere anion.[2] On the other hand, the same reaction of a cobalt(III) ammine complex is initiated by an electron transfer from the ligand or an outersphere anion to the central cobalt(III) ion.[3] In our previous paper,[4] it was shown that the thermal reactions of halogenopentaammine and *cis*-dihalogenotetraammineruthenium(III) were initiated by the repalcement of coordinated ammonia by the outersphere halide ion in the cases of chloride and bromide, while the reaction was initiated by the ammonia release, without the substitution reaction, for iodoammine iodide compounds. Trehoux and his coworkers[5] estimated the product, $[RuCl(NH_3)_5]Cl_2$, in the course of the thermal decomposition of $[Ru(NH_3)_6]Cl_3$; however, there is no information on any kinetic studies of the reactions.

In the present paper, kinetic studies of the thermal substitution reactions of $[Ru(NH_3)_6]X_3$ and *cis*-$[RuX_2(NH_3)_4]X$ will be demonstrated and the reaction mechanisms will be discussed in comparison with those of analogous chromium(III) ammine complexes.

Experimental

Preparation of Complexes. The complexes, $[Ru(NH_3)_6]X_3$, (X=Br, I) and $[RuX_2(NH_3)_4]X$, (X=Cl, Br, I), were prepared by the methods described in the literature.[6,7] The complexes were confirmed by elemental analyses and by the visible and UV spectra. Found: H, 4.26; N, 19.25%. Calcd for $[Ru(NH_3)_6]Br_3$: H, 4.05; N, 18.92%. Found: H, 3.27; N, 14.54%. Calcd for $[Ru(NH_3)_6]I_3$: H, 3.08; N, 14.39%. Found: H, 4.67; N, 18.97%. Calcd for $[RuCl_2(NH_3)_4]Cl \cdot 2/5\ H_2O$: H, 4.53; N, 19.80%. Found: H, 2.91; N, 13.82%. Calcd for $[RuBr_2(NH_3)_4]Br$: H, 2.94; N, 13.70%. Found: H, 2.09; N, 10.23%. Calcd for $[RuI_2(NH_3)_4]I$: H, 2.18; N, 10.18%.

Derivatographic and Isothermal Kinetic Study. The differential thermal analysis (DTA) curves of the complexes were obtained by means of a Shimadzu D. T. 20B micro-differential thermal analyzer, while the thermogravimetric measurement was carried out using a Shimadzu T.G.C.20-type micro-thermobalance. All the experiments were made in a helium atmosphere at the heating rate of 5 °C/min, using 3—5 mg of the sample for each run.

From the results of isothermal thermogravimetry, the kinetic plot—the time conversion curves of the mass-loss were plotted at several constant temperatures. In this experiment, the temperature was rapidly elevated so as to pyrolyze the sample in a platinum cell placed in a furnace, the temperature was kept constant within ±0.5 °C.

A Hitachi 323 recording spectrophotometer was used for the measurement of the absorption spectra of the initial compounds and of the reaction products.

Results and Discussion

DTA and TG Studies. The DTA and TG curves of the hexaammineruthenium(III) trihalides are given in Fig. 1. Those of the *cis*-dihalogenotetraammine

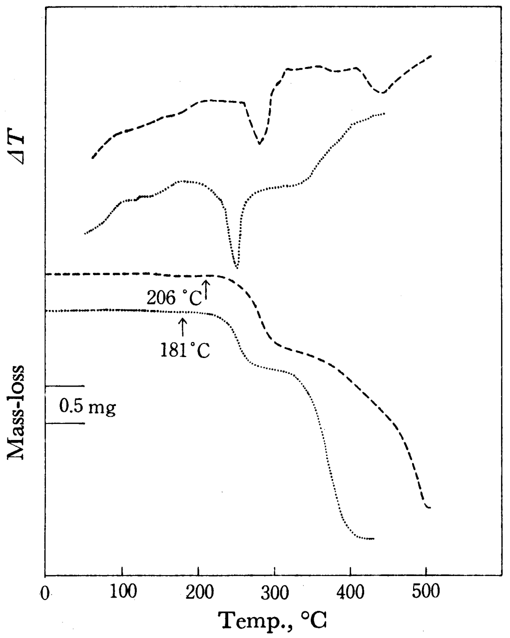

Fig. 1. DTA and TG curves of $[Ru(NH_3)_6]X_3$ in a helium atmosphere.
----: $[Ru(NH_3)_6]Br_3$, ····: $[Ru(NH_3)_6]I_3$

complexes have already been exhibited in a previous paper.[4] The DTA curves are characterized by endothermic peaks — at 280 °C (tribromide) and 251 °C (triiodide); these peaks correspond well to the first mass-loss on the TG curves. Similar results have been obtained for the cases of the *cis*-dihalogenocomplexes. The ranges of the reaction temperature were selected by reference to the results of DTA and TG studies.

Stoichiometry and Kinetic Study. The thermal decomposition products were one mole of ammonia and halogenopentaammine halide per mole of hexaammine halides in the region of the selected temperature. Thus, the thermal decomposition reaction can be expressed by Eq. (1):

$$[\mathrm{Ru(NH_3)_6}]\mathrm{X_3} \longrightarrow \mathrm{NH_3} + [\mathrm{RuX(NH_3)_5}]\mathrm{X_2}, \quad (\mathrm{X=Br,\ I}) \quad (1)$$

On the other hand, one mole of *cis*-dihalogenotetraammine halides was decomposed to form one mole of ammonia and trihalogenotriammines. The latter product was identified as the *trans*-isomer from the results of the UV and IR spectra measurements.[8,9]

$$cis\text{-}[\mathrm{RuX_2(NH_3)_4}]\mathrm{X} \longrightarrow \mathrm{NH_3} + trans\text{-}[\mathrm{RuX_3(NH_3)_3}], \quad (\mathrm{X=Cl,\ Br}) \quad (2)$$

In the thermal decomposition of *cis*-diiodotetraammine iodide, Reaction 3 has already been reported:[4]

$$cis\text{-}[\mathrm{RuI_2(NH_3)_4}]\mathrm{I} \longrightarrow 4\mathrm{NH_3} + \mathrm{RuI_3} \quad (3)$$

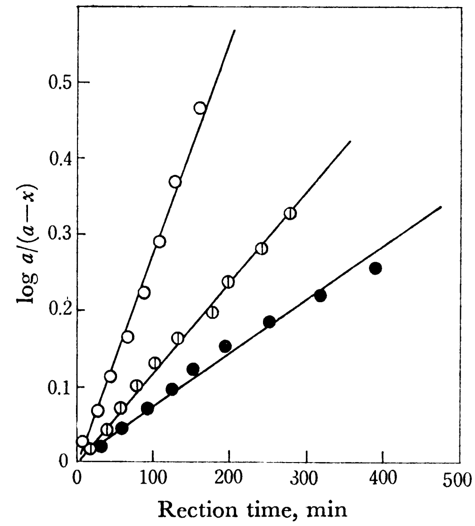

Fig. 2. Plots of a first-order rate equation for the deammonation-anation reaction of *cis*-$[\mathrm{RuBr_2(NH_3)_4}]$Br.
—○—: 179°C, —⦶—: 166°C, —●—: 162°C

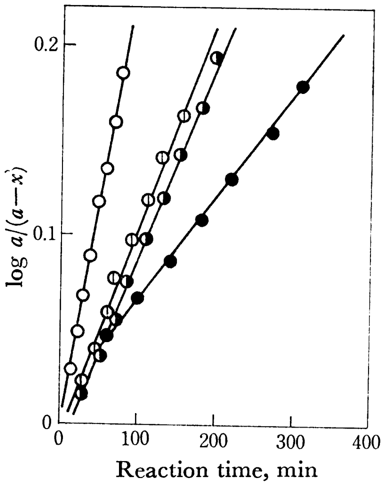

Fig. 3. Plots of a first-order rate equation for the deammonation-anation reactions of $[\mathrm{Ru(NH_3)_6}]\mathrm{Br_3}$.
—○—: 185°C, —⦶—: 177°C, —◑—: 172°C, —●—: 161°C

Table 1. Rate constants and kinetic parameters of the deammonation-anation reactions for Ru(III) and Cr(III)[2] ammine complexes

Reaction	$k\times10^5$ s^{-1} (Temp., °C)	E_a (kcal/mol)	$\Delta S^{\neq}$ (e.u.)	Frequency factor A, s^{-1}
$[\mathrm{Cr(NH_3)_6}]\mathrm{Cl_3}\rightarrow[\mathrm{CrCl(NH_3)_5}]\mathrm{Cl_2}+\mathrm{NH_3}$	2.97 (170)	30	−12	
$[\mathrm{Ru(NH_3)_6}]\mathrm{Br_3}\rightarrow[\mathrm{RuBr(NH_3)_5}]\mathrm{Br_2}+\mathrm{NH_3}$	2.10 (161)			
	3.92 (172)			
	4.17 (177)			
	9.21 (185)	23.3	−29.3	9.97×10^6
$[\mathrm{Cr(NH_3)_6}]\mathrm{Br_3}\rightarrow[\mathrm{CrBr(NH_3)_5}]\mathrm{Br_2}+\mathrm{NH_3}$	2.16 (192)	43	12	
$[\mathrm{Ru(NH_3)_6}]\mathrm{I_3}\rightarrow[\mathrm{RuI(NH_3)}]_5\mathrm{I_2}+\mathrm{NH_3}$	4.52 (144)			
	6.02 (151)			
	11.25 (158)			
	13.07 (164)	20.7	−31.6	3.06×10^6
$[\mathrm{Cr(NH_3)_6}]\mathrm{I_3}\rightarrow\mathrm{CrN}+3\mathrm{NH_4I}+2\mathrm{NH_3}$	3.0 (204)	49	18	
cis-$[\mathrm{RuCl_2(NH_3)_4}]\mathrm{Cl}\rightarrow[\mathrm{RuCl_3(NH_3)_3}]+\mathrm{NH_3}$	2.04 (163)			
	2.72 (166)			
	4.98 (172)			
	7.78 (179)	33.1	−6.9	8.01×10^{11}
cis-$[\mathrm{RuBr_2(NH_3)_4}]\mathrm{Br}\rightarrow[\mathrm{RuBr_3(NH_3)_3}]+\mathrm{NH_3}$	2.92 (162)			
	4.48 (166)			
	5.16 (168)			
	11.73 (179)	31.3	−10.1	1.55×10^{11}
cis-$[\mathrm{RuI_2(NH_3)_4}]\mathrm{I}\rightarrow\mathrm{RuI_3}+4\mathrm{NH_3}$		28		
cis-$[\mathrm{CrCl_2(NH_3)_4}]\mathrm{Cl}\rightarrow[\mathrm{CrCl_3(NH_3)_3}]+\mathrm{NH_3}$	11.0 (136)	31	−2	

All the reaction products were identified by elemental analysis and/or absorption spectrophotometry. A detailed report on the stereoisomers of trihalogenotriammine will be published elsewhere.

Plots of $\log a/(a-x)$ *vs.* the reaction time for Reactions 1 and 2 are exemplified by those of *cis*-$[RuBr_2(NH_3)_4]Br$ and $[Ru(NH_3)_6]Br_3$ in Figs. 2 and 3, where "a" is the initial mass of the sample and where "$a-x$" is the mass at the reaction time, t. The plot gives a straight line with a good reproducibility for each kinetic measurement. Similar relationships were obtained for the other complexes. As a result, the thermal decomposition reaction can be regarded as a first-order reaction with respect to the reactant. The rate constant obtained from the slope of the straight line is listed in Table 1.

Arrhenius plots for the reactions are given in Fig. 4, while the kinetic parameters are listed in Table 1. The activation energy for the *cis*-diiodotetraammine iodide was determined by a graphic analysis of the Freeman-Carroll equation.

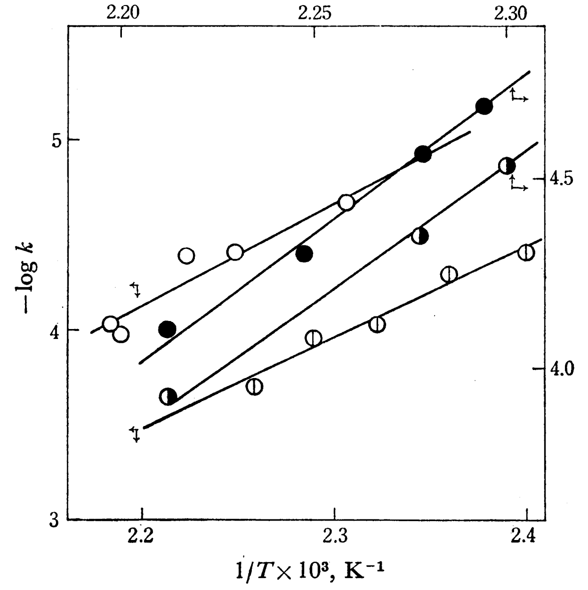

Fig. 4. Arrhenius plots of the substitution reactions for *cis*-$[RuX_2(NH_3)_4]X$, and $[Ru(NH_3)_6]X_3$.
cis-$[RuX_2(NH_3)_4]X$······●: Cl, ◑: Br
$[Ru(NH_3)_6]X_3$······○: Br, ⦶: I

It can be seen that the rate constant for the deammonation reaction of hexaammine bromide is smaller than that of the hexaammine iodide. On the other hand, the rate constant for the *cis*-dichlorotetraammine chloride is smaller than that of the dibromotetraammine bromide. The influence of outersphere anion species is to enhance the reaction rate in the following order: $Cl<Br<I$.

By a comparison of the two series of complexes, it was found that the rate constant for the hexaammine halide is smaller than that of dihalogenotetraammine; however, the relation between the activation energies for the two series of complexes is inconsistent with that of the rate constants. Furthermore, the values of the activation entropy for the former series are smaller than those for the latter series. These facts suggest that there are some differences in the reaction mechanisms for the deammonation and the anation of the outersphere anion. The entering of an outersphere halide anion into the coordination-sphere is more difficult for the dihalogeno-complex halide because of the repulsion by the already-coordinated halide ligands.

Reaction Mechanism of the Deammonation-anation. For the sake of comparison, the kinetic data for the substitution reaction of the ruthenium(III) ammines are listed again, along with those for the chromium(III) ammines, in Table 1. Nagase and Tanaka[2] have demonstrated that the substitution reaction of the $[Cr(NH_3)_6]Cl_3$ complex proceeds according to the S_N2-type mechanism, while the same reaction of the bromide and iodide takes place *via* the S_N1-type mechanism. The appearances of the reactions of ruthenium(III) ammine halides are entirely different from those for the chromium(III) ammine complexes. The rate of the substitution reaction for ruthenium hexaammine iodide is about five times faster than that for the bromide. For the chromium hexaammine halide, the largest rate is found in the case of hexaammine chloride. The reaction of hexaammine iodide is different from those of chloride and bromide, and the rate is the smallest of the three compounds.

For the tetraammine series of complexes, the rate for

TABLE 2. THE INITIATION TEMPERATURE OF DEAMMONATION AND THE WAVE NUMBER OF Ru–N STRETCHING VIBRATION,[6] ν_{Ru-N} (cm^{-1}) FOR RUTHENIUM(III) AMMINE COMPLEXES

Complex	X					
	Cl		Br		I	
	Temp., °C	ν	Temp., °C	ν	Temp., °C	ν
$[Ru(NH_3)_6]X_3$	200[a]	474	206	472	181	468
		464		461		457
		452		450		448
$[RuX(NH_3)_5]X_2$[b]	246	485	244	479	174	468
		463		459		450
		451		448		442
						424
cis-$[RuX_2(NH_3)_4]X$	200	—	210	—	114	—

a) Unpublished work. b) Ref. 4.

the chromium(III) complex is much larger than that of the ruthenium(III) complex. Considering the small values of the activation energy and the negative values of the activation entropy, the mechanism for the reaction of hexaammineruthenium(III) halides seems to belong to the S_N2 category. On the other hand, for the dihalogeno complex halide the S_N1-like mechanism may be most probable. This is the most important difference in comparison with the chromium(III) complexes.(2)

The contribution of the π-bonding nature between the metal and the ligand may be considered to account for the mechanisms of the hexaammine and dihalogenotetraammine complexes. Basolo and Pearson(10) have described how the halide ion is a stronger electron-donor rather than an ammonia molecule through the π bond from ligand to metal. The electron-donating ligand makes it possible to dissociate other ligands at the *cis* or *trans* position and to increase the reaction rate by putting more negative charge on the metal. Thus, the halide ligands in the tetraammine halide are more effective in facilitating a S_N1 mechanism for the deammonation-anation reaction than the ammine ligand in the hexaammine halide.

The initiation temperatures of the deammonation reactions for the three series of ruthenium(III) ammine complexes are listed in Table 2, along with the data of the infrared spectra. If the thermal stability of a complex is reflected in the initiation temperature, the compounds containing the iodide ion are generally less stable. When the number of iodide ions in the innersphere increases, the thermal stability of the complex decreases. One of the reasons for this may be a weakening of the strength of the ruthenium-ammine bond by the increase in the covalency of the ruthenium-halide bond. This consideration is supported by the fact that the wave number of the Ru–N stretching vibration decreases upon the replacement of the ammine ligand by the iodide ion.

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