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Thermal Reactions of Metal Complexes under Quasi-isothermal and -isobaric Conditions. II.1) Formation of Triamminetrihalogenochromium(III) Complexes *via* the Decomposition of Hexaammine, Pentaamminehalogeno, and *trans*-Tetraamminedihalogeno Complexes2)

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The thermal decomposition of the following chromium(III) complexes was investigated in the solid phase by means of Q-derivatograph under quasi-isothermal and -isobaric conditions (Q-conditions) and D-derivatograph under dynamic conditions (D-conditions): $[Cr(NH_3)_6]X_3$, $[CrX(NH_3)_5]Y_2$, and *trans*-$[CrX_2(NH_3)_4]Y$, where X and Y are chloride and/or bromide ions. The complexes were finally converted into triamminetrihalogeno complexes $[CrBr_xCl_y(NH_3)_3]$ ($x+y=3$; x and $y=0$, 1, 2, or 3) under Q-conditions but decomposed in complicated ways under D-conditions. All the triamminetrihalogeno complexes thus obtained have *mer*-configuration with respect to the positions of the three halide ions.

Methods for preparing triamminetrihalogenochromium(III) complexes are usually based on the use of $[Cr(O_2)_2(NH_3)_3]$ in aqueous media3) or that of thermal decomposition of ammine complexes in open systems.4) However, the former is considerably troublesome while the latter has the disadvantage that thermal reactions in open systems do not always proceed uniformly to give pure products. The thermal reactions of metal complexes have been reported to proceed reproducibly and uniformly under quasi-isothermal and -isobaric conditions (Q-conditions),1) and the intermediates and the final products in each reaction step can be obtained in remarkably pure constitution.5)

This paper deals with the investigation of (1) the thermal decomposition of various amminechromium(III) complexes under Q-conditions as well as dynamic conditions (D-conditions)1) and (2) the possibility of the formation of triamminetrihalogeno complexes.

The reactions in this work are classified as follows according to the final products: (A) Formation of $[CrCl_3(NH_3)_3]$ from $[Cr(NH_3)_6]Cl_3$, $[CrCl(NH_3)_5]Cl_2$, and *trans*-$[CrCl_2(NH_3)_4]Cl$; (B) formation of $[CrBr_3(NH_3)_3]$ from $[Cr(NH_3)_6]Br_3$ and $[CrBr(NH_3)_5]Br_2$; (C) formation of $[CrBrCl_2(NH_3)_3]$ from $[CrBr(NH_3)_5]Cl_2$, *trans*-$[CrCl_2(NH_3)_4]Br$, and *trans*-$[CrBrCl(NH_3)_4]Cl$; and (D) formation of $[CrBr_2Cl(NH_3)_3]$ from $[CrCl(NH_3)_5]Br_2$ and *trans*-$[CrBrCl(NH_3)_4]Br$.

Experimental

Preparation of Complexes. The complexes except for the mixed halogeno complexes were prepared according to known procedures.

$[Cr(NH_3)_6]Cl_3$ (I),6) $[Cr(NH_3)_6]Br_3$ (II),7) and $[CrCl(NH_3)_5]Cl_2$ (III)8) were obtained by the methods reported.

$[CrCl(NH_3)_5]Br_2$ (IV) was prepared by adding NaBr to an aqueous solution of $[CrCl(NH_3)_5]Cl_2$ (III).

trans-$[CrCl_2(NH_3)_4]Cl$ (V) and *trans*-$[CrCl_2(NH_3)_4]Br$ (VI) were obtained by the acid cleavage of rhodochromic chloride $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Cl_5$.9)

$[CrBr(NH_3)_5]Br_2$ (VII) was prepared by the method of Linhard and Weigel.10)

$[CrBr(NH_3)_5]Cl_2$ (VIII) was obtained by the addition of NH_4Cl to $[CrBr(NH_3)_5]Br_2$ (VII) in ice-cooled water.

trans-$[CrBrCl(NH_3)_4]Cl$ (IX) and *trans*-$[CrBrCl(NH_3)_4]Br$ (X): Chloroerythrochromic bromide $[(NH_3)_5Cr(OH)CrCl(NH_3)_4]Br_4$ prepared from the corresponding chloride9) was added to a mixture of 60% $HClO_4$ and concd HBr (2: 1) in a loosely stoppered flask. The mixture was left to stand at room temperature for 2 h. The solid product was collected and washed with a small amount of 1 M $HClO_4$. Bright green *trans*-$[CrBrCl(NH_3)_4]ClO_4$ thus obtained was converted into *trans*-$[CrBrCl(NH_3)_4]Cl\cdot nH_2O$ and *trans*-$[CrBrCl(NH_3)_4]Br\cdot nH_2O$ with a saturated solution of NH_4Cl and concd HBr, respectively, and then collected and dried at 100 °C for 5 and 2 h to give the anhydrous chloride and bromide, respectively. Analytical data for the mixed halogeno complexes are given in Table 1.

Measurements. The thermal reactions were traced on MOM D- and Q-derivatographs.1) Measurements by D-derivatograph were carried out in a constant flow of nitrogen at heating rate 1 °C min^{-1}. The electronic spectra were measured in powder state with a Hitachi EPU-2A spectrophotometer equipped with a standard Hitachi reflection attachment (Type R-3).

TABLE 1. ANALYTICAL DATA FOR STARTING COMPLEXES

Complex	H (%)		N (%)		Cr (%)	
	Found	Calcd	Found	Calcd	Found	Calcd
$[CrCl(NH_3)_5]Br_2$ (IV)	4.60	4.51	21.08	21.05	15.32	15.64
$[CrBr(NH_3)_5]Cl_2$ (VIII)	5.31	5.21	24.23	24.31	17.91	18.05
trans-$[CrCl_2(NH_3)_4]Br$ (VI)	4.47	4.43	20.66	20.66	18.97	19.18
trans-$[CrBrCl(NH_3)_4]Cl$ (IX)	4.63	4.43	20.43	20.66	19.22	19.18
trans-$[CrBrCl(NH_3)_4]Br$ (X)	3.85	3.80	17.83	17.75	16.26	16.48

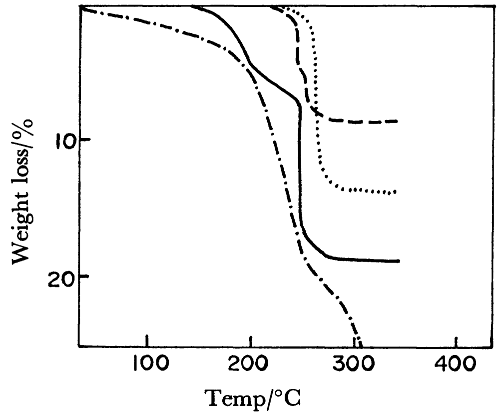

Fig. 1. Q-derivatograms of complexes I (——), III (······), and V (---) together with D-derivatogram of complex I (—·—).

Results and Discussion

Formation of Triamminetrihalogeno Complexes. *(A) Formation of* $[CrCl_3(NH_3)_3]$ *from* $[Cr(NH_3)_6]Cl_3$ *(I),* $[CrCl(NH_3)_5]Cl_2$ *(III), and* trans-$[CrCl_2(NH_3)_4]Cl$ *(V).* Figure 1 shows the Q-derivatograms of complexes I, III, and V together with the D-derivatogram (TG curve only) of complex I. As seen from the D-derivatogram of complex I, a monotonous decrease takes place and no plateau is obtained in the TG curve, indicating that the complex decomposes gradually in a complicated manner with no formation of uniform products. Since this tendency was found in all the other complexes, their D-derivatograms are omitted in the following discussion.

On the other hand, the Q-derivatogram of complex I shows a gradual weight loss at 150—242 °C due to the evolution of 1 mol of ammonia (Found: 7.61%; Calcd: 6.52%), and then an abrupt weight loss takes place at 242 °C until a plateau is attained. The total weight loss is 18.69% approximately agreeing with that (19.58%) calculated for the formation of $[CrCl_3(NH_3)_3]$. The original yellow color turned green at this stage. The results suggest that complex I undergoes deammonation to be converted into $[CrCl_3(NH_3)_3]$ *via* $[CrCl(NH_3)_5]Cl_2$ without forming $[CrCl_2(NH_3)_4]Cl$.

The Q-derivatogram of complex III shows rapid evolution of 2 mol of ammonia in a narrow temperature range (250—260 °C), after which a clear plateau is obtained, the complex turning green from red. The net weight loss (13.77%) coincides with the value calculated for the formation of $[CrCl_3(NH_3)_3]$ (13.99%).

In the Q-derivatogram of complex V, a sharp change in weight takes place nearly isothermally (230—250 °C) until a distinct plateau appears. The weight loss in 7.73% which is close to that (7.50%) calculated for 1 mol of ammonia.

The analytical data for the triamminetrihalogeno complexes are summarized in Table 2. The observed and calculated values agree, indicating that $[CrCl_3(NH_3)_3]$ is obtained under Q-conditions irrespective of the starting complex.

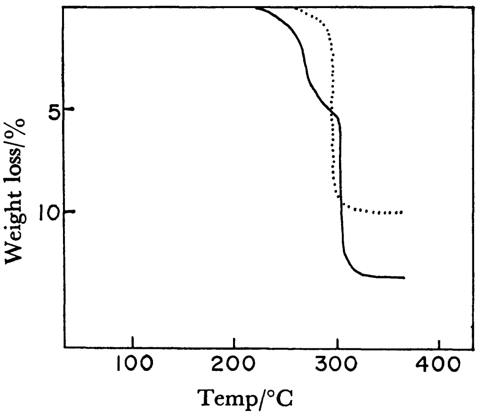

Fig. 2. Q-derivatograms of complexes II (——) and VII (······).

TABLE 2. ANALYTICAL DATA FOR TRIAMMINETRIHALOGENO COMPLEXES PRODUCED

( ): Calcd

Triammine complex	Starting complex	H (%)	N (%)	Cr (%)
(A) *mer*-$[CrCl_3(NH_3)_3]$	$[Cr(NH_3)_6]Cl_3$	4.19 (4.29)	19.78 (20.04)	24.69 (24.82)
	$[CrCl(NH_3)_5]Cl_2$	4.24 (4.29)	20.01 (20.04)	24.84 (24.82)
	trans-$[CrCl_2(NH_3)_4]Cl$	4.30 (4.29)	19.61 (20.04)	25.02 (24.82)
(B) *mer*-$[CrBr_3(NH_3)_3]$	$[Cr(NH_3)_6]Br_3$	2.53 (2.62)	11.82 (12.24)	14.64 (15.16)
	$[CrBr(NH_3)_5]Br_2$	2.40 (2.62)	12.29 (12.24)	14.95 (15.16)
(C) *mer*-$[CrBrCl_2(NH_3)_3]$	$[CrBr(NH_3)_5]Cl_2$	3.50 (3.54)	16.40 (16.54)	20.50 (20.47)
	trans-$[CrCl_2(NH_3)_4]Br$	3.52 (3.54)	16.91 (16.54)	20.31 (20.47)
	trans-$[CrBrCl(NH_3)_4]Cl$	3.61 (3.54)	16.70 (16.54)	20.15 (20.47)
(D) *mer*-$[CrBr_2Cl(NH_3)_3]$	$[CrCl(NH_3)_5]Br_2$	2.99 (3.02)	14.61 (14.09)	17.66 (17.42)
	trans-$[CrBrCl(NH_3)_4]Br$	3.07 (3.02)	14.23 (14.09)	17.52 (17.42)

(B) Formation of $[CrBr_3(NH_3)_3]$ *from* $[Cr(NH_3)_6]Br_3$ *(II) and* $[CrBr(NH_3)_5]Br_2$ *(VII).* Figure 2 shows the Q-derivatograms of complexes II and VII. They give patterns similar to those of the foregoing chlorides I and III, respectively. The first gradual weight loss for complex II (250—303 °C) is due to the evolution of 1 mol of ammonia (Found: 4.95%; Calcd: 4.31%) and the second rapid weight loss is due to the evolution of 2 mol of ammonia. The TG curve then reaches a plateau. The overall weight loss (12.50%) agrees with that (12.94%) calculated for the formation of $[CrBr_3(NH_3)_3]$.

Complex VII gives only one rapid weight loss step corresponding to the liberation of 2 mol of ammonia (Found: 8.97%; Calcd: 9.02%). The formation of $[CrBr_2(NH_3)_4]Br$ was not detectable in the decomposition pathways of both the complexes.

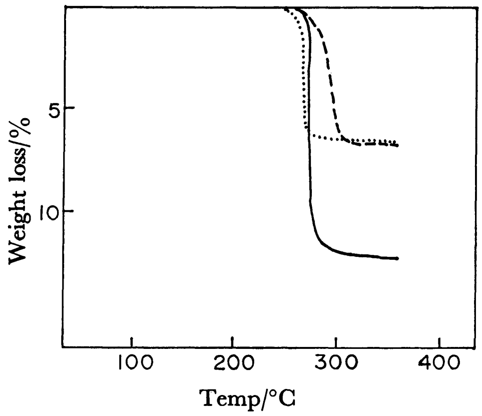

Fig. 3. Q-derivatograms of complexes VIII (——), VI (······), and IX (---).

(C) Formation of $[CrBrCl_2(NH_3)_3]$ *from* $[CrBr(NH_3)_5]Cl_2$ *(VIII),* trans-$[CrCl_2(NH_3)_4]Br$ *(VI), and* trans-$[CrBrCl(NH_3)_4]Cl$ *(IX).* The Q-derivatograms of complexes VIII, VI, and IX are shown in Fig. 3. Complex VIII evolves 2 mol of ammonia nearly isothermally (275—285 °C), and complexes VI and IX, 2 mol of ammonia at 267—280 °C and 253—290 °C, respectively. The observed weight loss due to the evolution of ammonia is 11.62% (Calcd: 11.81%) for complex VIII, 6.26% (Calcd: 6.27%) for complex VI and 6.34% (Calcd: 6.27%) for complex IX. The analytical data indicate that all the final products have exactly the same composition as $[CrBrCl_2(NH_3)_3]$ (Table 2).

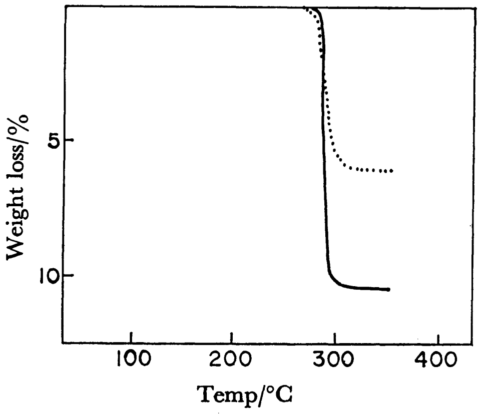

Fig. 4. Q-derivatograms of complexes IV (——) and X (······).

(D) Formation of $[CrBr_2Cl(NH_3)_3]$ *from* $[CrCl(NH_3)_5]Br_2$ *(IV) and* trans-$[CrBrCl(NH_3)_4]Br$ *(X).* We see from Fig. 4 that complexes IV and X evolve 2 mol (Found: 5.46%; Calcd: 5.39%) and 1 mol (Found: 10.26%; Calcd: 10.22%) of ammonia, respectively, at 270—290 °C to form $[CrBr_2Cl(NH_3)_3]$.

Configuration of Triamminetrihalogeno Complexes Obtained. Two configurations are possible for the triamminetrihalogeno complexes, facial and meridional with respect to the positions of the three halide ions (or three ammonia molecules). Such distinction in $[CrX_3N_3]$ chromophore (X denotes halide ion and N nitrogen atom) has been achieved from electronic spectral measurements.[4a,11] *fac*-Form has two bands, whereas *mer*-form has three in d-d transition region, a weak band due to the spin-forbidden transition ($^4A_{2g} \rightarrow {}^2E_g$) appearing in lower wavelength region ($\approx 13 \times 10^3$ cm^{-1}) being characteristic of *mer*-form.

Figures 5—8 show the electronic spectra of $[CrCl_3(NH_3)_3]$, $[CrBr_3(NH_3)_3]$, $[CrBrCl_2(NH_3)_3]$, and $[CrBr_2Cl(NH_3)_3]$. The triamminetrihalogeno complexes obtained from *trans*-dihalogeno complexes have the

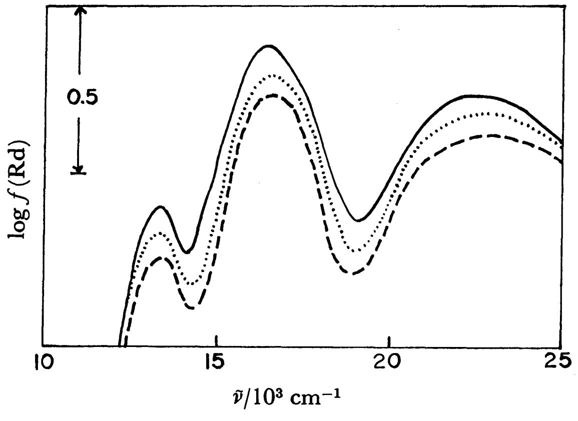

Fig. 5. Electronic spectra of $[CrCl_3(NH_3)_3]$ produced from complexes I (——), III (······), and V (---).

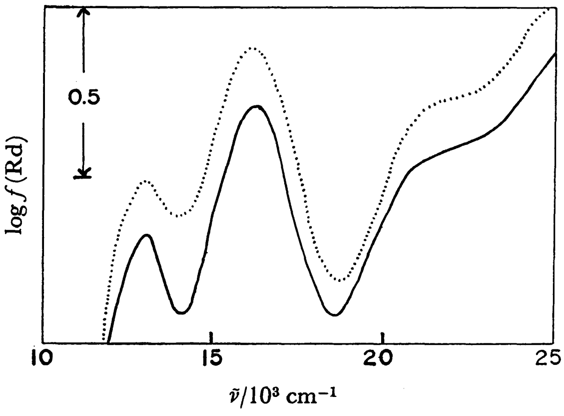

Fig. 6. Electronic spectra of $[CrBr_3(NH_3)_3]$ produced from complexes II (——) and VII (······).

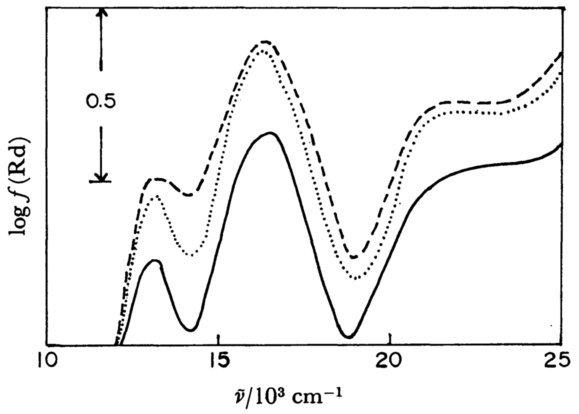

Fig. 7. Electronic spectra of $[CrBrCl_2(NH_3)_3]$ produced from complexes VIII (——), VI (······), and IX (---).

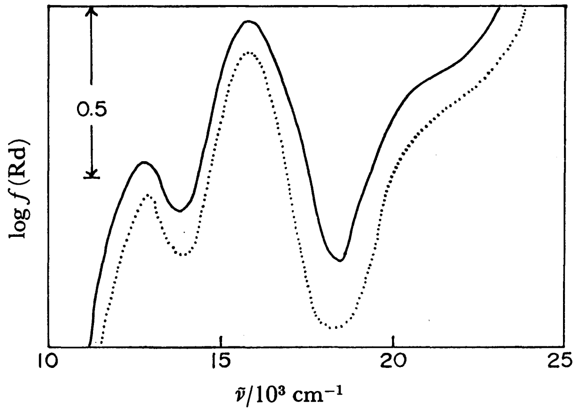

Fig. 8. Electronic spectra of $[CrBr_2Cl(NH_3)_3]$ produced from complexes IV (——) and X (······).

possibility to take only *mer*-configuration. All the spectra have one weak and two strong bands, indicating that all the triamminetrihalogeno complexes are in *mer*-configuration.

TABLE 3. ABSORPTION MAXIMA FOR TRIAMMINETRIHALOGENO COMPLEXES

Complex	Maxima ($^4A_{2g} \rightarrow {}^2E_g$) $\tilde{\nu}$/cm^{-1}	Maxima ($^4A_{2g} \rightarrow {}^4T_{2g}$) $\tilde{\nu}$/cm^{-1}
mer-$[CrCl_3(NH_3)_3]$	13400	16700
mer-$[CrBrCl_2(NH_3)_3]$	13100	16200
mer-$[CrBr_2Cl(NH_3)_3]$	12900	16000
mer-$[CrBr_3(NH_3)_3]$	12800	15600

The absorption maxima due to $^4A_{2g}\rightarrow{}^2E_g$ and $^4A_{2g}\rightarrow{}^4T_{2g}$ transitions are given in Table 3. The absorption maxima due to $^4A_{2g}\rightarrow{}^4T_{2g}$ are shifted to the lower energy region according to spectrochemical series in the order $[CrCl_3(NH_3)_3]\rightarrow[CrBrCl_2(NH_3)_3]\rightarrow[CrBr_2Cl(NH_3)_3]\rightarrow[CrBr_3(NH_3)_3]$. Two structures are possible for *mer*-$[CrBrCl_2(NH_3)_3]$ and *mer*-$[CrBr_2Cl(NH_3)_3]$: *viz.*, *cis*-form and *trans*-form regarding chloride and bromide ions, but the question is still pending.

Summary of Thermal Reaction Pathways. The hexaammine complexes are converted into pentaamminehalogeno and then triamminetrihalogeno complexes without forming tetraamminedihalogeno complexes. The pentaamminehalogeno complexes undergo deammonation in one step to yield triamminetrihalogeno complexes, without forming tetraamminedihalogeno complexes. Why no tetraamminedihalogeno complexes can be produced in the reaction pathways of hexaammine and pentaammine complexes is easily understandable from a comparison of the formation temperature of triamminetrihalogeno complexes:

$[CrCl(NH_3)_5]Cl_2 \longrightarrow [CrCl_3(NH_3)_3]$	250—270 °C
trans-$[CrCl_2(NH_3)_4]Cl \longrightarrow [CrCl_3(NH_3)_3]$	230—250 °C
$[CrBr(NH_3)_5]Cl_2 \longrightarrow [CrBrCl_2(NH_3)_3]$	275—285 °C
trans-$[CrBrCl(NH_3)_4]Cl \longrightarrow [CrBrCl_2(NH_3)_3]$	253—273 °C
$[CrCl(NH_3)_5]Br_2 \longrightarrow [CrBr_2Cl(NH_3)_3]$	290—300 °C
trans-$[CrBrCl(NH_3)_4]Br \longrightarrow [CrBr_2Cl(NH_3)_3]$	270—290 °C.

The temperatures of the tetraamminedihalogeno complexes are lower than those of the corresponding pentaamminehalogeno complexes. Thus, even though the tetraamminedihalogeno complexes are produced in each reaction pathway, they are immediately decomposed, forming triamminetrihalogeno complexes.

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