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THERMAL DECOMPOSITION OF THE OXO- AND HYDROXO-BRIDGED BINUCLEAR CHROMIUM(III) COMPLEXES.
Part I. Kinetics and mechanism of the processes

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ABSTRACT

Experimental results are reported for the determination of the decomposition mechanism of oxo- and hydroxo-bridged binuclear ammine complexes of Cr(III) under non-isothermal conditions. Kinetic parameters of the process have been determined according to the relationship of Freeman and Carroll.

INTRODUCTION

The rhodo- and erythro-binuclear ammine complexes of Cr(III) were first prepared by Jørgensen in 1882 [1]. Several papers have been devoted to explaining their exact constitution, unusual acid–base isomerization behavior, reaction kinetics [2–7], electronic structures, magnetic susceptibilities [8–12] and electrical properties [14].

Wilmarth et al. [3], on the basis of their careful analysis, determination of pK values, and cleavage-reaction studies of these compounds, proposed the following formulae and relationships for these binuclear complexes of chromium(III):

$$[(NH_3)_5Cr{-}OH{-}Cr(NH_3)_5]^{5+}$$

Rhodochromic ion

$$\underset{H^+}{\overset{OH^-}{\rightleftharpoons}} [(NH_3)_5Cr{-}O{-}Cr(NH_3)_5]^{4+}$$

Basic rhodochromic ion

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$$[(NH_3)_5Cr{-}OH{-}Cr(H_2O)(NH_3)_4]^{5+}$$

Erythrochromic ion

$$\underset{OH^-}{\overset{H^+}{\rightleftharpoons}} [(NH_3)_5Cr{-}OH{-}Cr(OH)(NH_3)_4]^{4+}$$

Basic erythrochromic ion

X-Ray studies of these complexes have also been reported [13,15,16]. In these binuclear complexes of chromium(III), the basic rhodochromic salts have been reported to have very different properties from the other compounds in the series. These unusual properties of the basic rhodochromic complex have been ascribed to the fact that the Cr–O–Cr system may be linear, while the other complexes in these series may have the bent Cr–OH–Cr bridge [16]. Therefore, the differences during decomposition have been investigated in this work. The thermal dissociation of ammonia complexes of chromium(III) salts has been extensively investigated [17–22], but there are no data concerning the thermal decomposition of binuclear chromium(III)–ammine complexes with oxo and hydroxo bridges.

EXPERIMENTAL

The compounds μ-oxo-bis {pentaamminechromium(III)} chloride (basic rhodochromic chloride) monohydrate, $[Cr_2O(NH_3)_{10}]Cl_4 \cdot H_2O$ and pentaamminechromium(III)-μ-hydroxoaquotetraamminechromium(III) chloride (erythrochromic chloride), $[Cr_2OH(NH_3)_9H_2O]Cl_5$, were prepared from μ-hydroxo-bis {pentaamminechromium(III)} chloride (rhodochromic chloride), $[Cr_2OH(NH_3)_{10}]Cl_5$ as previously described [1,2].

A 1500 Derivatograph (MOM Budapest) was used for the experiments. Samples ranged in mass from 100 to 260 mg and were pyrolysed in an air atmosphere at a heating rate of $10\,^\circ C\ min^{-1}$ in the temperature range 20–1000 °C.

The X-ray analysis was performed on a Dron-2 diffractometer using Co,Fe-filtered radiation (10°–60° range).

RESULTS AND DISCUSSION

The results of the DTA-TG-DTG studies on the $[Cr_2OH(NH_3)_{10}]Cl_5$ complex are given in Fig. 1.

The DTA curve of the $[Cr_2OH(NH_3)_{10}]Cl_5$ complex contained a well-defined endothermic peak with a peak maximum temperature of 205 °C, followed by a broad endothermic peak with a peak maximum at about

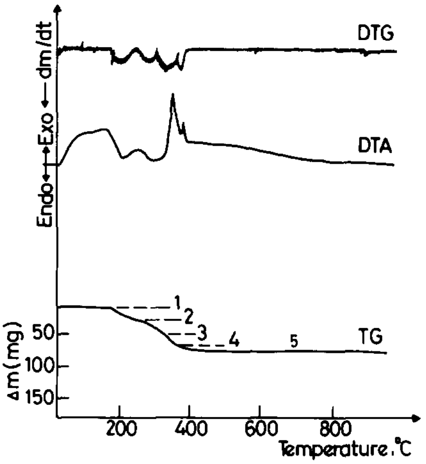

Fig. 1. Results of simultaneous DTA-TG-DTG analysis for $[Cr_2OH(NH_3)_{10}]Cl_5$ in air atmosphere at a heating rate of 10 °C min^{-1}: 1, $[Cr_2OH(NH_3)_{10}]Cl_5$; 2, $[Cr(NH_3)_3Cl_3]+[CrOH(NH_3)Cl_2]$; 3, $CrCl_3+CrOHCl_2$; 4, $Cr_2O_3+CrOHCl_2$; 5, Cr_2O_3.

320 °C. The first peak was due to evolution of 6 mol of ammonia with the formation of $Cr(NH_3)_3Cl_3$ and $CrOH(NH_3)Cl_2$ according to the reaction

$$[Cr_2OH(NH_3)_{10}]Cl_5 \longrightarrow Cr(NH_3)_3Cl_3 + CrOH(NH_3)Cl_2 + 6NH_3 \qquad (1)$$

The remaining 4 mol ammonia were evolved during the second endothermic peak, according to the reactions

$$\begin{aligned} Cr(NH_3)_3Cl_3 &\longrightarrow CrCl_3 + 3NH_3 \\ CrOH(NH_3)Cl_2 &\longrightarrow Cr(OH)Cl_2 + NH_3 \end{aligned} \qquad (2)$$

The competition of these two reactions was examined by analysis of the pyrolysis residue. The ratios of Cr : Cl indicated the relative amounts of the complex which had been decomposed by the two processes. The amount of ammonia was found from the mass-loss data (Table 1).

TABLE 1

Mass-loss data for $[Cr_2OH(NH_3)_{10}]Cl_5$

Reaction	Mass loss (mg)		Temperature range (°C)	Type of transformation
	Theor.	Exp.		
(1)	21.8	22.5	180–267	Endo
(2)	14.4	15.0	267–320	Endo
(3)	21.0	20.0	320–375	Exo
(4)	16.0	15.0	375–400	Exo

TABLE 2

Identification of final product Cr_2O_3 by the X-ray method

Cr_2O_3 standard		Final product of thermal decomposition								
d (Å)	J/J_{100}	$[Cr_2OH(NH_3)_{10}]Cl_5$			$[Cr_2O(NH_3)_{10}]Cl_4 \cdot H_2O$			$[Cr_2OH(NH_3)_9H_2O]Cl_5$		
		2θ	d(Å)	J/J_{100}	2θ	d(Å)	J/J_{100}	2θ	d(Å)	J/J_{100}
		26.20	3.934	25				26.40	3.920	20
3.636	75	28.50	3.636	25	28.50	3.636	43	28.30	3.662	20
2.667	100	39.30	2.662	75	39.20	2.668	65	39.10	2.675	67
2.481	95	42.30	2.481	100	42.30	2.481	100	42.30	2.481	100
2.262	12									
2.174	40	48.70	2.171	50	48.50	2.179	43	48.50	2.179	67
2.049	10									
1.815	40	59.30	1.809	25	59.00	1.818	22	59.00	1.818	33

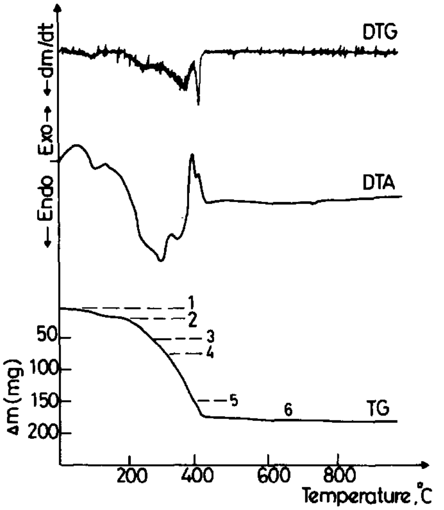

Fig. 2. Results of simultaneous DTA-TG-DTG analysis for $[Cr_2OH(NH_3)_9H_2O]Cl_5$ in air atmosphere at a heating rate of 10 °C min^{-1}: 1, $[Cr_2OH(NH_3)_9H_2O]$ Cl_5; 2, $[Cr_2OH(NH_3)_9Cl]Cl_4$; 3, $[Cr(NH_3)_3Cl_3+[CrOH(NH_3)_2Cl_2]$; 4, $CrOHCl_2+[Cr(NH_3)_3Cl_3]$; 5, $Cr_2O_3+CrCl_3$; 6, Cr_2O_3.

Above 320 °C exothermic oxidation of the intermediate $CrCl_3$ and $Cr(OH)Cl_2$ products was noted according to the reactions

$$2CrCl_3+\tfrac{3}{2}O_2 \longrightarrow Cr_2O_3+3Cl_2 \qquad (3)$$

$$2Cr(OH)Cl_2+\tfrac{1}{2}O_2 \longrightarrow Cr_2O_3+2HCl+Cl_2 \qquad (4)$$

The final product Cr_2O_3 in all these cases was identified by the X-ray method (see Table 2).

The DTA-TG-DTG thermogram of the $[Cr_2OH(NH_3)_9H_2O]Cl_5$ complex is given in Fig. 2.

The thermogram for erythrochromic chloride showed three endothermic peaks at 95, 295 and 340 °C, and two sharp exothermic peaks with maxima at 400 and 415 °C.

TABLE 3

Mass-loss data for $[Cr_2OH(NH_3)_9H_2O]Cl_5$

Reaction	Mass loss (mg)		Temperature range (°C)	Type of transformation
	Theor.	Exp.		
(5)	9.9	10.0	40–120	Endo
(6)	37.6	35.0	120–270	Endo
(7)	21.0	22.0	270–320	Endo
(8)	68.1	70.0	320–390	Exo
(9)	27.3	27.5	390–420	Exo

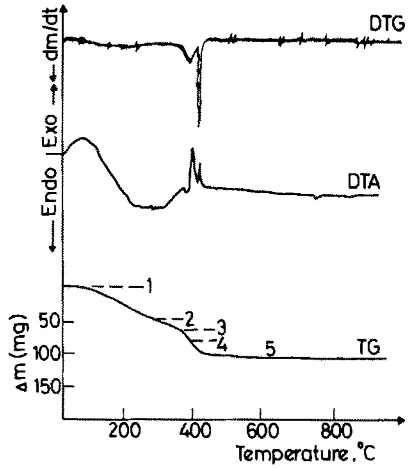

Fig. 3. Results of simultaneous DTA-TG-DTG analysis for $[Cr_2O(NH_3)_{10}]Cl_4 \cdot H_2O$ in air atmosphere at a heating rate of $10\,°C/min^{-1}$: 1, $[Cr_2O(NH_3)_{10}]Cl_4 \cdot H_2O$; 2, $[Cr(NH_3)_3Cl_3] + CrOCl$; 3, $CrOCl + CrCl_3$; 4, $Cr_2O_3 + CrOCl$; 5, Cr_2O_3.

The above phenomena may be explained by the reactions

$$[Cr_2OH(NH_3)_9H_2O]Cl_5 \longrightarrow [Cr_2OH(NH_3)_9Cl]Cl_4 + H_2O \tag{5}$$

$$[Cr_2OH(NH_3)_9Cl]Cl_4 \begin{array}{l} \nearrow Cr(NH_3)_3Cl_3 \\ \\ \searrow CrOH(NH_3)_2Cl_2 \end{array} + \; 4NH_3 \tag{6}$$

$$CrOH(NH_3)_2Cl_2 \longrightarrow Cr(OH)Cl_2 + 2NH_3 \tag{7}$$

$$\left.\begin{array}{l} 2Cr(OH)Cl_2 + \frac{1}{2}O_2 \longrightarrow Cr_2O_3 + 2HCl + Cl_2 \\ Cr(NH_3)_3Cl_3 \longrightarrow CrCl_3 + 3NH_3 \end{array}\right. \tag{8}$$

$$2CrCl_3 + \frac{3}{2}O_2 \longrightarrow Cr_2O_3 + 3Cl_2 \tag{9}$$

The amount of ammonia, chloride and hydrogen chloride were found from the mass-loss data given in Table 3.

The DTA-TG-DTG curves for the $[Cr_2O(NH_3)_{10}]Cl_4 \cdot H_2O$ complex are given in Fig. 3 and in general are similar to those mentioned above, except for the initial dehydration reaction

$$[Cr_2O(NH_3)_{10}]Cl_4 \cdot H_2O \begin{array}{l} \rightarrow Cr(NH_3)_3Cl_3 \\ \searrow CrOCl \end{array} + 7NH_3 + H_2O \tag{10}$$

At the first stage of the decomposition of $[Cr_2O(NH_3)_{10}]Cl_4 \cdot H_2O$ complex, in addition to $Cr(NH_3)_3Cl_3$ [20], CrOCl [18,22] is formed.

At the next stage of decomposition, the triamine complex loses three molecules of ammonia to give chromium(III) chloride according to

$$Cr(NH_3)_3Cl_3 \longrightarrow CrCl_3 + 3NH_3 \tag{11}$$

Two well-defined exothermic peaks with maxima at 410 and 425 °C, corresponded to the evolution of chlorine by reactions (12) and (13), respectively.

$$2CrCl_3 + 3O_2 \longrightarrow Cr_2O_3 + 3Cl_2 \tag{12}$$

$$2CrOCl + \tfrac{1}{2}O_2 \longrightarrow Cr_2O_3 + Cl_2 \tag{13}$$

The final product Cr_2O_3 was identified by the X-ray method (Table 2). The mass-loss data of the $[Cr_2O(NH_3)_{10}]Cl_4 \cdot H_2O$ complex, calculated from the TG curve are given in Table 4.

In order to confirm the formation of the respective intermediate products during thermal decomposition, chlorine and chromium contents in the preheated samples were determined. The samples were each heated for 2 h at the defined temperature (corresponding to the decomposition temperature), and after that they were analyzed. The ratio of Cr : Cl indicated the relative amounts of the complex which had been decomposed by each process.

Based on the results from Figs. 1–3 using TG data from sample mass loss during heating, using the method of Freeman and Carroll [23], the following kinetic parameters were determined: activation energy (E) and reaction order (n) for the processes of thermal decomposition of $[Cr_2OH(NH_3)_{10}]Cl_5$, $[Cr_2OH(NH_3)_9H_2O]Cl_5$ and $[Cr_2O(NH_3)_{10}]Cl_4 \cdot H_2O$. From the Freeman and Carroll method they are related by

$$\frac{E/2.3R\ \Delta(1/T)}{\Delta \log m_r} = -n + \frac{\Delta \log \mathrm{d}m/\mathrm{d}\tau}{\Delta \log m_r} \tag{14}$$

where E is the activation energy, n the reaction order, R the universal gas constant, T the absolute temperature and m_r is the total mass loss. The kinetic results for the thermal decomposition of the studied chromium(III) ammine complexes, are shown in Figs. 4–6.

From the results shown in Fig. 4 for the thermal decomposition processes of $[Cr_2OH(NH_3)_{10}]Cl_5$, the following values for the activation energy have been determined: 7, 21, 2 and 18 kJ mol^{-1} for processes (1), (2), (3) and (4), respectively, with values of 0.9, 1.05, 1 and 0.8 for the reaction order. From the results shown in Fig. 5 for the thermal decomposition of

TABLE 4

Mass-loss data for $[Cr_2O(NH_3)_{10}]Cl_4 \cdot H_2O$

Reaction	Mass loss (mg)		Temperature range (°C)	Type of transformation
	Theor.	Exp.		
(10)	48.7	45.0	100–260	Endo
(11)	14.0	15.2	260–370	Endo
(12)	24.3	21.3	370–400	Exo
(13)	19.7	20.0	400–430	Exo

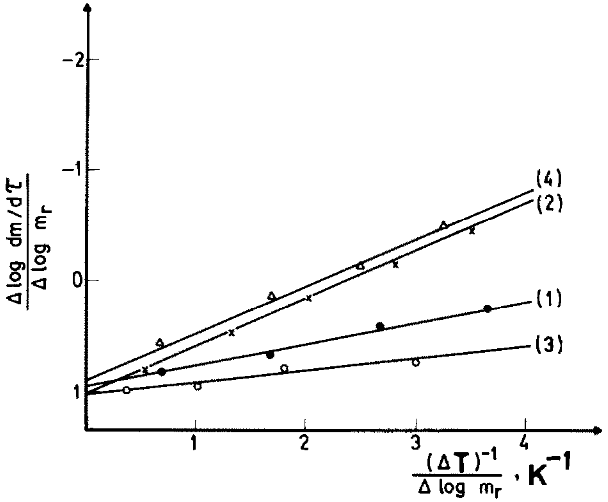

Fig. 4. Kinetics of decomposition of $[Cr_2OH(NH_3)_{10}]Cl_5$: 1, process (1); 2, process (2); 3, process (3); 4, process (4).

$[Cr_2OH(NH_3)_9H_2O]Cl_5$, the following values for activation energy have been determined: 106, 82, 150, 26 and 10 kJ mol^{-1} for processes (5), (6), (7), (8) and (9), respectively, with values for the reaction order of 1.4, 1.2, 1.1, 1 and 0.9. Results shown in Fig. 6 for the thermal decomposition of

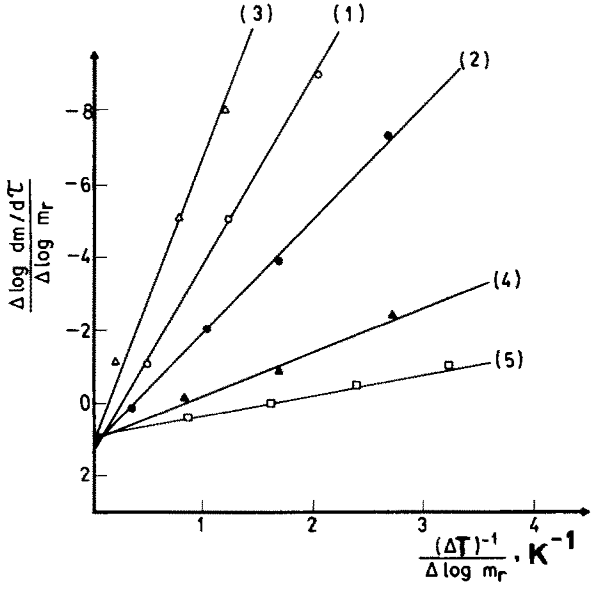

Fig. 5. Kinetics of decomposition of $[Cr_2OH(NH_3)_9H_2O]Cl_5$: 1, process (5); 2, process (6); 3, process (7); 4, process (8); 5, process (9).

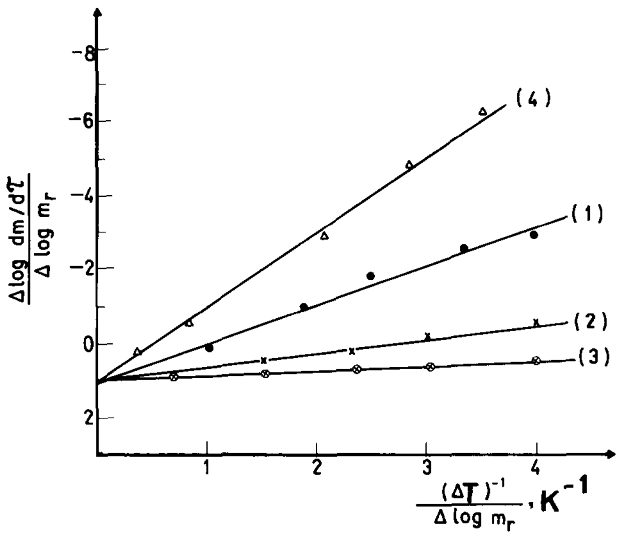

Fig. 6. Kinetics of decomposition of $[Cr_2O(NH_3)_{10}]Cl_4 \cdot H_2O$: 1, process (10); 2, process (11); 3, process (12); 4, process (13).

$[Cr_2O(NH_3)_{10}]Cl_4 \cdot H_2O$, gave the following values for activation energy: 49, 30, 4 and 83 kJ mol^{-1} for processes (10), (11), (12) and (13), respectively, with values for the reaction order of 1.2, 1, 0.8 and 1.

The results obtained from kinetic investigations of thermal decomposition processes of chromium(III) ammine complexes indicate that deammonation occurs under appropriate kinetic conditions for the cases of $[Cr_2OH(NH_3)_{10}]Cl_5$ and $[Cr_2O(NH_3)_{10}]Cl_4 \cdot H_2O$ decomposition. For $[Cr_2OH(NH_3)_9H_2O]Cl_5$, deammonation occurs after extraction of the H_2O molecule from the complex structure which means that the deammonation takes place under favourable kinetic conditions, since the bonds with ammonia in this structure are weakened. Oxidation of $CrCl_3$ to Cr_2O_3 in all three cases is limited by oxygen diffusion, while the oxidation of CrOCl and $CrOHCl_2$ takes place in a defined kinetic zone owing to the fact that part of the oxygen is already within the structure of these compounds. For all the chromium(III) complexes examined the final product of thermal decomposition in air atmosphere is Cr_2O_3 in crystal form.

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