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THE THERMAL DECOMPOSITION OF METAL COMPLEXES—IX

THE DIAQUOTETRAMMINE AND DIAQUOBIS(ETHYLENEDIAMINE) CHROMIUM(III) HALIDE COMPLEXES

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Abstract—The thermal dissociation of the chromium(III) complexes, $[Cr(NH_3)_4(H_2O)_2]X_3$ (X = Cl, Br) and $[Cr(en)_2(H_2O)_2]X_3 \cdot 2H_2O$ (X = Cl, Br), was studied by thermogravimetry and differential thermal analysis. For the chloride complex, water was evolved in a stepwise manner according to the reaction: $[Cr(NH_3)_4(H_2O)_2]Cl_2 \rightarrow [Cr(NH_3)_4Cl_2]Cl$. The $[Cr(en)_2(H_2O)_2]X_3 \cdot 2H_2O$ complexes lost all of their water in one step. The kinetics of several of the deaquation reactions were determined.

THE deaquation of the diaquotetrammine- and diaquo*bis*(ethylenediamine)chromium(III) halides was first noted by Pfeiffer in 1907.(1,2) It was observed that the orange colored $[Cr(NH_3)_4(H_2O)_2]Cl_3$ complex slowly changed into the red coloured $[Cr(NH_3)_4(H_2O)Cl]Cl_2$ on standing at room temperature. The process was accelerated at 100°C, where it was found that the deaquation was completed in about 30 min. Likewise, a similar colour change was noted for the $[Cr(en)_2(H_2O)_2]X_3 \cdot 2H_2O$ complexes which evolved water to give the monoaquo-complexes, $[Cr(en)_2(H_2O)X]X_2$.

In continuing our present work on the thermal dissociation of chromium(III) and other metal co-ordination compounds,(3,4) the thermal properties of the chromium (III) complexes, $[Cr(NH_3)_4(H_2O)_2]X_3$ (X = Cl, Br), and the *bis*(ethylenediamine)-chromium(III) complexes, $[Cr(en)_2(H_2O)_2]X_2 \cdot 2H_2O$ (X = Cl, Br), were investigated.

EXPERIMENTAL

Thermobalance. The automatic recording thermobalance has previously been described.(5) Sample sizes ranged in weight from 80 to 90 mg and were pyrolysed in a static air atmosphere at a furnace heating rate of 5–6°C per min.

Vacuum pyrolysis studies. The vacuum pyrolysis apparatus has previously been described.(4) Sample sizes ranged in weight from 90 to 100 mg and were pyrolysed to a maximum temperature of about 600°C. The composition of the evolved decomposition gases was determined by a mass spectrometer.

Differential thermal analysis apparatus. The apparatus which was employed has previously been described.(6) Sample sizes ranged in weight from 30 to 40 mg and were pyrolysed in a dynamic helium atmosphere at a heating rate of 10°C per min.

Preparation of complexes. The diaquotetramminechromium(III) halides were prepared from $[Cr(py)_2(H_2O)_2(OH)_2]X_2$ by the method previously described by PFEIFFER.(1)

The diaquo*bis*(ethylenediamine)chromium(III) halide 2-hydrates were prepared by the method previously described.(2)

The complexes were analysed for water content by desiccation and metal content by ignition of the complexes, mixed with oxalic acid, to 800°C in a muffle furnace.

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(2) P. PFEIFFER, *Z. Anorg. Chem.* **58**, 236 (1908).

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(5) W. W. WENDLANDT, T. D. GEORGE and G. R. HORTON, *J. Inorg. Nucl. Chem.* **17**, 274 (1961).

(6) W. W. WENDLANDT, *Analyt. Chim. Acta* **27**, 309 (1962).

RESULTS AND DISCUSSION

Diaquotetrammine- and diaquobis(ethylenediamine)chromium(III) complexes. The weight-loss curves for these compounds are given in Fig. 1.

The thermal dissociation curve of $[Cr(NH_3)_4(H_2O)_2]Cl_3$ indicated that water was evolved beginning at 70°C. Two breaks were observed in the curve, at 110 and 200°C, respectively. Based upon weight-loss data, the composition of the compounds present at these breaks was $[Cr(NH_3)_4(H_2O)Cl]Cl_2$ and $[Cr(NH_3)_4Cl_2]Cl$, respectively. Total decomposition of the latter compound began at 200°C, giving a residue of Cr_2O_3 beginning at about 500°C. It was of interest to note that the composition of the curve at 450°C approximated the composition, Cr(OH)O. Thus, the dissociation sequence appears to be:

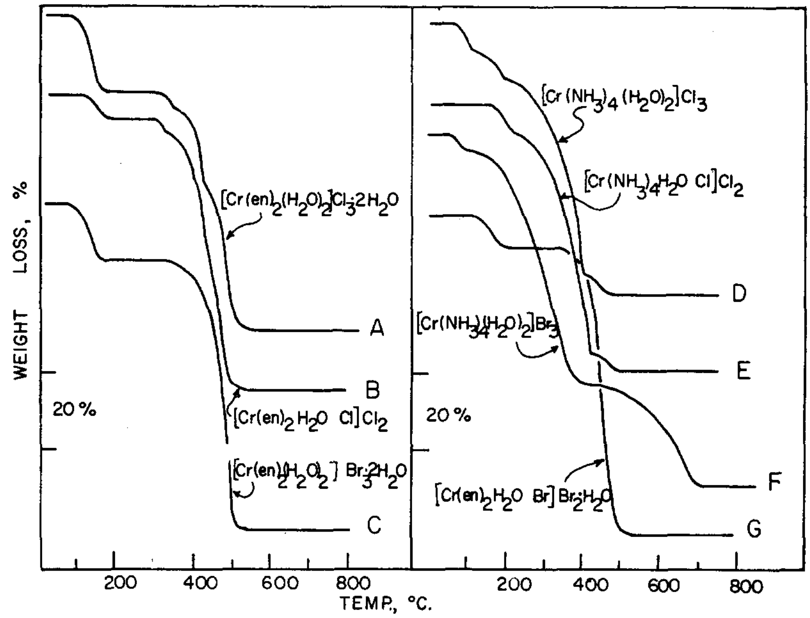

FIG. 1.—Weight-loss curves for chromium(III) complexes (in air).

A. $[Cr(en)_2(H_2O)_2]Cl_3{\cdot}2H_2O$
B. $[Cr(en)_2(H_2O)Cl]Cl_2$
C. $(Cr(en)_2(H_2O)_2]Br_3{\cdot}2H_2O$
D. $[Cr(NH_3)_4(H_2O)_2]Cl_3$
E. $[Cr(NH_3)_4(H_2O)Cl]Cl_2$
F. $[Cr(NH_2)_4(H_2O)_2]Br_3$
G. $[Cr(en)_2(H_2O)Br]Br_2{\cdot}H_2O$

$$[Cr(NH_3)_4(H_2O)_2]Cl_2(s) \rightarrow [Cr(NH_3)_4(H_2O)Cl]Cl_2(s) + H_2O(g)$$

$$[Cr(NH_3)_4(H_2O)Cl]Cl_2(s) \rightarrow [Cr(NH_3)_4Cl_2]Cl(s) + H_2O(g)$$

$$[Cr(NH_3)_4Cl_2]Cl \rightarrow Cr_2O_3 + \text{decomposition products.}$$

The curve for $[Cr(NH_3)_4(H_2O)Cl]Cl_2$ was identical to that for the above compound after the loss of the first mole of water.

The curve for $[Cr(NH_3)_4(H_2O)_2]Br_3$ showed that the first deaquation reaction began at about 70°C giving a break in the curve at about 100–110°C. However, no breaks were observed for the loss of the second mole of water as was found for the chloride. Although a break was noted in the curve at about 450°C, no definite stoicheiometry could be assigned to it. The terminal product of the pyrolysis was Cr_2O_3.

The weight-loss curve of $[Cr(en)_2(H_2O)_2]Cl_3{\cdot}2H_2O$ showed that the deaquation reaction began at about 75°C. All four moles of water were apparently evolved at the same time because no intermediate curve breaks were observed up to 200°C. However, due to the limitations of the thermobalance, the stepwise dissociation of the water molecules may not be detected in the weight-loss curve under the experimental conditions employed. Unequivocal proof of the structure of the compound cannot be made from TGA data alone. From the DTA curve for this compound, as shown in Fig. 2, there was a shoulder peak at about 115°C which may be due to the evolution of part of the water of hydration. Further weight-loss above 310°C gave the Cr_2O_3 weight level at about 550°C.

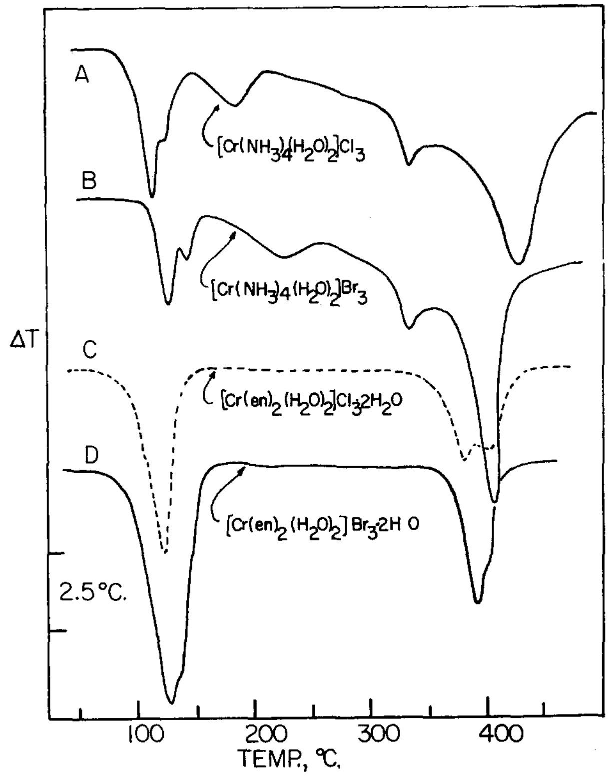

FIG. 2.—DTA curves of chromium (III) complexes (in helium).
A. $[Cr(NH_3)_4(H_2O)_2]Cl_3$ C. $[Cr(en)_2(H_2O)_2]Cl_3{\cdot}2H_2O$
B. $[Cr(NH_3)_4(H_2O)_2]Br_3$ D. $[Cr(en)_2(H_2O)_2]Br_3{\cdot}2H_2O$

The compound, $[Cr(en)_2(H_2O)Cl]Cl_2$, gave a weight-loss curve which was similar to that for the diaquo-complex except that the deaquation reaction began at a higher temperature, about 125°C.

The weight-loss curve for $[Cr(en)_2(H_2O)_2]Br_3{\cdot}2H_2O$ was similar to that found for the analogous chloride complex except that the first weight-loss began at about 70°C. Further decomposition above 350°C gave the Cr_2O_3 weight level beginning at about 550°C.

The weight-loss behaviour of $[Cr(en)_2(H_2O)Br]Br_2{\cdot}H_2O$ was similar to that found for the diaquobromide complex except that the deaquation reaction began at a higher temperature, 125°C. The terminal decomposition product was Cr_2O_3 in all cases.

The differential thermal analysis (DTA) curves for the above complexes are given in Fig. 2.

The DTA curve for $[Cr(NH_3)_4(H_2O)_2]Cl_3$ showed that the deaquation reactions took place below 200°C. Two peaks, with peak maxima temperatures of 115° and 180°C, respectively, and also a shoulder peak at 125°C, were due to the deaquation reaction. Further decomposition of $[Cr(NH_3)_4Cl_2]Cl$ gave endothermic peaks at 330° and 425°C, respectively.

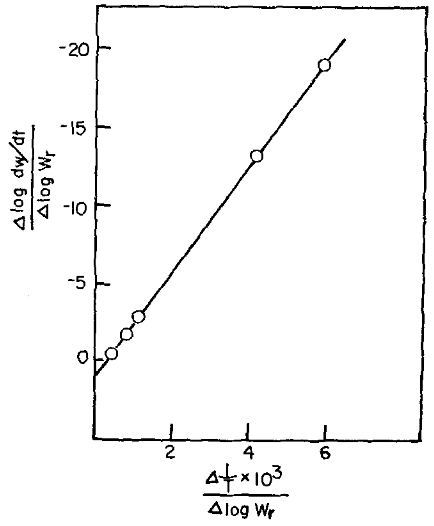

Fig. 3.—Freeman and Carroll kinetics plot for $[Cr(en)_2(H_2O)_2]Br_3 \cdot 2H_2O$ (air atmosphere).

The behaviour of $[Cr(NH_3)_4(H_2O)_2]Br_3$ was similar to that for the analogous chloride compound. The shoulder peak was more resolved for the first water evolution while there was a broad endothermic peak for the evolution of the second mole of water. The decomposition of $[Cr(NH_3)_4Br_2]Br$ gave endothermic peaks at 330° and 405°C, respectively. Since all of the curves were determined in a helium atmosphere, the terminal decomposition product was the chromium(III) halide.

The DTA curves for the complexes, $[Cr(en)_2(H_2O)_2]Cl_3 \cdot 2H_2O$ and $[Cr(en)_2(H_2O)_2]Br_3 \cdot 2H_2O$, were very similar to each other. The first endothermic peak was due to the deaquation of the four moles of water while the second peak was due to the dissociation of the $[Cr(en)_2X_2]X$ type complexes.

In an attempt to elucidate the composition of the pyrolysis products formed by these complexes, samples were pyrolyzed in a vacuum system and the gaseous products analyzed with a mass spectrometer. For the $[Cr(NH_3)_4(H_2O)_2]X_3$ type complexes, only water and ammonia could be detected. The $[Cr(en)_2(H_2O)_2]X_3 \cdot 2H_2O$ type complexes gave water, ammonia, ethylene, nitrogen and hydrogen. Free carbon and the chromium(III) halide were present in the sample pyrolysis boat.

Using the non-isothermal kinetics method of Freeman and Carrol,(7) the kinetics of the deaquation of several of the complexes was determined. A typical kinetics plot, for $[Cr(en)_2(H_2O)_2]Br_3 \cdot 2H_2O$, is illustrated in Fig. 3. The activation energies,

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(7) E. S. Freeman and B. Carroll, *J. Phys. Chem.* **62**, 394 (1958).

E_a, and reaction order so obtained were: $[Cr(en)_2(H_2O)_2]Cl_3 \cdot 2H_2O$, 18 ± 2 kcal, 1; $[Cr(en)_2(H_2O)Cl]Cl_2$, 15 ± 2, 1; $[Cr(en)_2(H_2O)_2]Br_3 \cdot 2H_2O$, 12 ± 2, 1; and $[Cr(en)_2(H_2O)Br]Br_2 \cdot H_2O$, 13 ± 2, 1. In all cases, a first order reaction was obtained with little change in activation energies in going from the chloride to bromide complexes. Judging from the errors involved in the determination of these values, the slight change in activation energies cannot be considered to be significant. The magnitude of the activation energies was similar to those obtained for the $[Cr(NH_3)_5(H_2O)]X_3$ ($X = Cl$, I, and NO_3) type complexes.(3)

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