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DERIVATOGRAPHIC THERMOANALYSIS OF $[Co(NH_3)_5Cl]Cl_2$

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ABSTRACT

Simultaneous TG, DTG, DTA and TGT (thermogravimetric titration) measurements using a MOM-derivatograph and a thermo-gas-titrimeter show that the complex $[Co(NH_3)_5Cl]Cl_2$ (I) decomposes in a static air atmosphere. In the first step three NH_3 molecules are lost. This step overlaps with a second step where the fourth NH_3 molecule is lost; the fifth NH_3 molecule is lost in the third step. A part of the fourth NH_3 molecule reduces Co(III) to Co(II) forming NH_4Cl and N_2. Pure $CoCl_2$ with almost theoretical yield is obtained at 510 ° C. A melting endotherm of $CoCl_2$ appears at 730 ° C and has a $\Delta H_f^{\ominus}$ value of -310.8 ± 0.7 kJ mol^{-1}. The final decomposition product is pure cobalt metal. A kinetic study of the first decomposition step of complex **I** gives value of kinetic constants (apparent or procedural) of $n = 0.5$ and $E_a = 124.64$ and 129.42 kJ mol^{-1} (depending on the method of calculation); values of log Z are 10.9 and 20.9 (Z in s^{-1}). The root mean square deviation (for ten E_a measurements within the first step) is 1.8%.

INTRODUCTION

An excellent monograph on the thermal properties of transition metal ammine complexes has been compiled by Wendlandt and Smith [1]. A detailed discussion of transition metal ammine complexes can also be found in Wendlandt [2] and Duval [3] and in the references therein. According to these sources the most widely investigated compound of the $[Co(NH_3)_5X]X_2$ series (where X = halogen) is chloropentammino-cobaltic chloride, perhaps because it is the most convenient precursor for the preparation and production of anhydrous $CoCl_2$.

According to the literature surveyed [1–6] the mechanism of decomposition of $[Co(NH_3)_5Cl]Cl_2$ (**I**) depends on instrumental and sample factors. For instance, in an atmosphere of ammonia this complex starts to decompose at 200 ° C and $CoCl_2$ and metallic cobalt form at 500 ° C and 700 ° C,

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respectively. The ammonia molecules are eliminated in one step. In nitrogen, the elimination of ammonia occurs in two steps. Other references [1–3] infer that in static air decomposition of the complex begins at 170 ° C; $CoCl_2$ and Co_3O_4 form at 360 ° C and 645 ° C, respectively, and metallic cobalt is absent. All heating programmes in these references were conducted on samples of about 100 mg at heating rates of about 5 ° C min^{-1}. However, certain information cannot be obtained from refs. 1–6, e.g. no simultaneous TG, DTG, DTA and TGT (thermogravimetric titration) measurements are available, no adequate explanation is given for the reduction of Co(III) to Co(II), some kinetic constants (such as log Z) for the first decomposition step are missing, other parameters (n and E_a) do not seem adequately informative, no information is given on the precision and accuracy of the measurements and so on. Our investigations have shown that with larger specimen weights (500–600 mg) and higher heating rates (10 ° C min^{-1}) in static air the five NH_3 molecules of complex **I** are lost in three decomposition steps instead of two as stated above. In addition no Co_3O_4 can be detected and no sublimation of $CoCl_2$ observed [4]. This paper constitutes an extension of the previous studies of complex **I** [1–4] using simultaneous TG, DTG, DTA and TGT curves.

EXPERIMENTAL

The TG, DTG, DTA and TGT curves were simultaneously generated on a MOM derivatograph and thermo-gas-titrimeter. Table 1 shows the instrumental parameters.

The heating programme used was ambient to 1050 ° C. The TGT curve was generated as instructed in the manufacturer's pamphlet. Supplementary techniques such as X-ray diffractometry and IR spectrophotometry were used as needed. All reagents were commercially available.

TABLE 1

Instrumental parameters

Sample weight	530 mg (finely ground)
Crucible	Platinum, open, cylindrical, MOM No. 3
Heating rate	10 ° C min^{-1}
Atmosphere	Static air
Reference material	α-alumina (activated at 1300 ° C for 2 h)
Sensitivity:	
TG	500 mg
DTG	1/10
DTA	1/10

RESULTS AND DISCUSSION

Thermal decomposition study

The decomposition of complex **I** has been the subject of much controversy. In particular, disagreement exists on how the ammonia molecules are lost, on the types of intermediates and final products, and on the kinetic and thermodynamic data which vary with different experimental conditions. Data obtained from Fig. 1 show that complex **I** starts to lose ammonia gas at 220 °C and this loss continues until about 22.6 wt.% has decomposed. This is equivalent to a release of three NH_3 molecules plus a part of another NH_3 molecule (see Table 2.) The remaining part of the fourth NH_3 molecule represents the second step of decomposition. The two partially overlapped steps are seen as a large, sharp, steep endotherm on the DTA curve with a small shoulder. The section from ambient temperature to 220 °C most probably represents the induction period for delayed nucleus formation; after a sufficient amount of nuclei have formed, the decomposi-

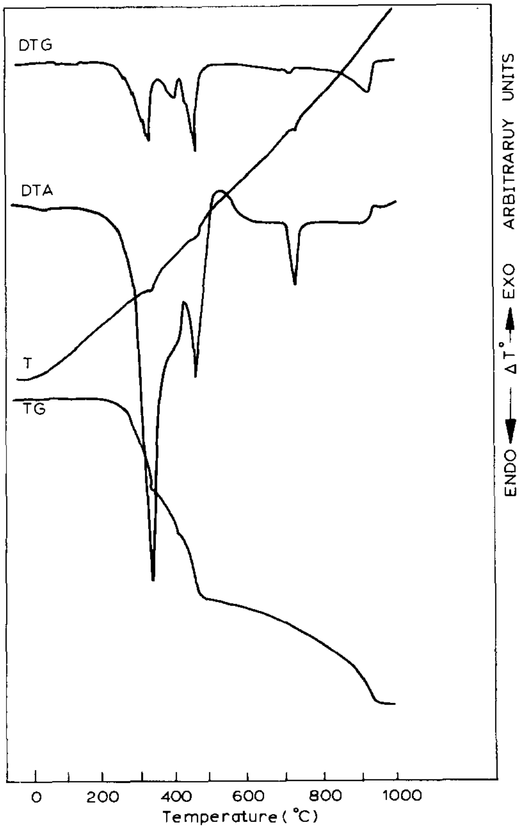

Fig. 1. Simultaneous TG-DTG-DTA-TGT of $[Co(NH_3)_5Cl]Cl_2$ in static air.

TABLE 2

Weight losses and temperature data of complex I in static air

Decomposition step	Wt. loss (%)		Decomposition temperature (°C)		$\Delta T^{\circ}_{\mathrm{min}}$ (°C)	Solid products	
	Theoretical	Experimental	T_i	T_f		Intermediate	Final
First	20.2	22.6	220	340	330	$[Co(NH_3)_{2-x}Cl]Cl_2$	–
Second	6.70	4.66	380	430	410	$[Co(NH_3)Cl]Cl_2$	–
Third	6.70	6.70	430	510	470	$CoCl_2$	–
Fourth	42.47	42.62	510	930	910	–	Co
Total	76.07	76.58	–	–	–	–	Co

tion takes place within a very narrow range of temperature. As the decomposition proceeds the concentration of NH_3 gas can build up around the decomposing solid, retarding the decomposition and temporarily inhibiting the escape of part of the fourth NH_3 molecule; a secondary redox reaction occurs resulting in the reduction of Co(III) to Co(II) and the formation of N_2 and NH_4Cl. It seems that the accumulated ammonia gas initiates some sort of self-generation of ammonia by displacing static air; therefore the prevailing reducing atmosphere is suitable for the simultaneous polymerization of complex **I** and the subsequent reduction of Co(III). The TGT curve (not shown) indicates that part of the ammonia which reduces the trivalent cobalt to the bivalent metal is itself oxidized to N_2. We detected N_2 as a decomposition by-product (no other workers have reported N_2 as a by-product). Although previous work [3] was carried out in ammonia we found similar intermediates and final products in static air but with different decomposition mechanisms, which can be represented as

$$6[Co(NH_3)_5Cl]Cl_2 \xrightarrow{\Delta} 6(CoCl_2 \cdot NH_4Cl \cdot NH_3) + 16NH_3 + N_2 \qquad (1)$$

$$6(CoCl_2 \cdot NH_4Cl \cdot NH_3) \xrightarrow{\Delta} 6CoCl_2 \cdot NH_3 + 6NH_4Cl \qquad (2)$$

$$6CoCl_2 \cdot NH_3 \xrightarrow{\Delta} 6CoCl_2 + 6NH_3 \qquad (3)$$

In contrast with the findings of some authors [1–4], we were unable to detect Co_3O_4 on heating complex **I** in static air. Equation 3 and the smaller sharp endotherm ($\Delta T^{\circ}_{\mathrm{min}} = 460\,^{\circ}C$) indicate the escape of the fifth NH_3 molecule. The partial separation of the fourth NH_3 molecule, as exhibited by the shoulder in Fig. 1, suggests that the Co–NH_3 bond may be strengthened because of the decreased steric crowding in complex **I** which allows a closer approach of NH_3 to Co. No explanation can be offered for the mechanism of disruption of the N–H bond and the subsequent formation of N_2. Autocatalysis may play a role here by lowering the activation energy of the reducing NH_3.

The formation of anhydrous $CoCl_2$ is enhanced by the presence of dissociated NH_4Cl ($NH_3 + HCl$) [3]. As expected no $CoCl_3$ is detected. At 510 °C the crucible contains $CoCl_2$ only. At 600 °C this starts to decompose gradually ($Co + Cl_2$) (Table 2) (autocatalysed by traces of freshly formed cobalt). At $\Delta T^{\circ}_{\min} = 730\,^{\circ}C$ the sharp melting endotherm of $CoCl_2$ is observed [7]. The molar enthalpy [12] of melting of $CoCl_2$ is found to be -310.8 ± 0.7 kJ mol^{-1} (the literature value [7] is -311.8 ± 0.23 kJ mol^{-1}). The boiling point of $CoCl_2$ is 1053°C [7]. The small endothermic peak at 720 °C indicates the enhancement of degradation of $CoCl_2$ during melting. Thereafter degradation continues and is complete at 930 °C, where only cobalt metal powder remains in the crucible. A comparison (Table 2) of the theoretical (76.07%) and the experimental (76.58%) weight losses indicates error of 0.51%. This accuracy complies with the allowed error of conventional thermogravimetry, and at the same time confirms the high accuracy of the results obtained.

Calculations show that the experimental yield of $CoCl_2$ is identical with the theoretical value; therefore complex I may be considered to be an excellent precursor for the preparation of $CoCl_2$.

Thermokinetic study

The apparent order n of the first decomposition step is found to be 0.5 [8–10]. This indicates that the chemical kinetics of this step are complex (see DTG curve) and are significantly influenced by the extent of accumulation of gaseous ammonia in the vicinity of the sample. Therefore only an apparent activation energy E_a of reaction can be calculated. The loss of the fourth NH_3 molecule (overlapping first and second steps) exhibits signs of temporary inhibition. This is because the repeated measurements of E_a increase with an increase in the fraction of decomposed ammonia [11].

The values of E_a (for the 220–340 °C step, when an overall weight loss of 23.21 wt.% occurs) are 124.64 kJ mol^{-1} using the Coats–Redfern method [8] and 129.42 kJ mol^{-1} using the Horowitz–Metzger methods [9].

The low value of $n = 0.5$ does not support a diffusion mechanism for the decomposition step studied. Surprisingly, for the same value of n, different values of log Z (Z in s^{-1}), i.e. 10.9 and 20.73, are obtained using refs. 8 and 9 respectively.

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