Journal of Thermal Analysis, Vol. 41 (1994) 99-104

THERMAL DECOMPOSITION OF HEXAMMINE-COBALT(III) CHLORIDE

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(Received December 2, 1992, in revised form March 12, 1993)

Abstract

The results of comparative thermal analysis (TG-DTG-DTA-DSC) of the thermal decomposition of hexamminecobalt(III) chloride in air atmosphere are reported. The kinetics and mechanism of the thermal decomposition, the process enthalpy and the variation in specific thermal capacity of the solid product reaction with temperature were determined.

Keywords: complexes, hexamminecobalt(III) chloride, kinetics, TG-DTG-DTA-DSC

Introduction

The thermal decompositions of amminecobalt(III) complexes have been studied by several authors [1–6]. The published data relate to the thermal decompositions of $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4H_2O$, but the results obtained are not complete.

As concerns the thermal decomposition of hexamminecobalt(III) chloride, recent studies [5, 6] have presented data obtained in air and argon atmospheres, but the data on the process mechanism are not compatible with data obtained in a previous investigation [1], and the differences have not been explained.

The present paper reports the results of comparative investigations of the thermal decomposition of hexamminecobalt(III) chloride by means of simultaneous DTA-TG-DTG analysis under nonisothermal conditions in air atmosphere. For determination of the enthalpies of the processes and the C_p change of the solid product reaction, use was made of DSC measurements.

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Experimental

The sample of hexamminecobalt(III) chloride was of p.a. purity; it was synthetized by Kemika, Zagreb. Thermal analysis was carried out on a derivatograph 1500, (MOM, Budapest, Hungary), and DSC analysis on a DSC-404 apparatus (NETZSCH). All analyses were performed in air atmosphere.

Results and discussion

Figure 1 illustrates results of simultaneous DTG-TG-DTG analysis of hexamminecobalt(III) chloride at a heating rate of 10 deg·min^{-1} in air atmosphere. From the mass loss results for certain processes (with an error less than 3%), for the heating rate interval 2.5 to 20 deg·min^{-1}, the following mechanism of thermal decomposition of $[Co(NH_3)_6]Cl_3$ was determined:

$$6\ [Co(NH_3)_6]Cl_3 \rightarrow 3\ CoCl_2 + 3\ (NH_4)_2CoCl_4 + N_2 + 28\ NH_3 \quad (1)$$

$$3\ (NH_4)_2CoCl_4 \rightarrow 6\ NH_4Cl + 3\ CoCl_2 \quad (2)$$

$$6\ CoCl_2 + 4\ O_2 \rightarrow 2\ Co_3O_4 + 6\ Cl_2 \quad (3)$$

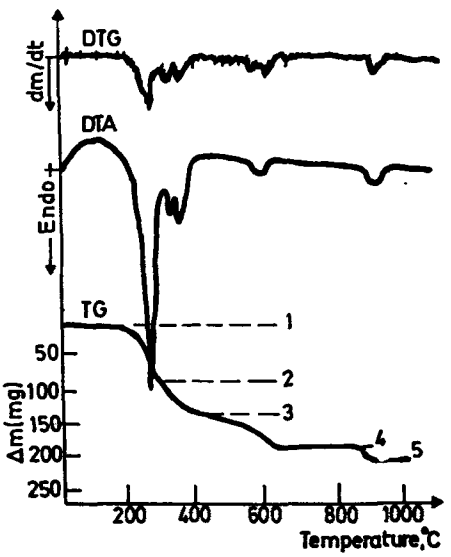

Fig. 1 The results of simultaneous DTA-TG-DTG analysis for $[Co(NH_3)_6]Cl_3$ in air atmosphere at heating rate of 10 deg·min^{-1}
(1 - $[Co(NH_3)_6]Cl_3$; 2 - $CoCl_2$+$(NH_4)_2CoCl_4$; 3 - $CoCl_2$; 4 - Co_3O_4; 5 - CoO)

$$Co_3O_4 \rightarrow 3\ CoO + 0.5\ O_2 \quad (4)$$

On the basis of the DTA results in air atmosphere at heating rates of 2.5 to 20 deg·min^{-1}, the kinetic parameters for the mechanism of thermal decomposition of hexamminecobalt(III) chloride were determined according to the method developed by Kissinger [7]. The DTA results obtained at different heating rates ate presented in Table 1.

Table 1 DTA results for the process of thermal decomposition of hexamminecobalt(III)-chloride at different heating rates

Processes	Heating rate, deg·min^{-1} T_m/°C			
	2.5	5	10	20
(1)	250	265	278	285
(2)→a	290	320	360	390
(2)→b	325	360	390	420
(3)	640	655	622	665
(4)	835	850	865	880

The results reveal that at these heating rates in the temperature interval 180–280°C, the thermal decomposition of $[Co(NH_3)_6]Cl_3$ involves the loss of nitrogen and ammonia, with formation of solid $CoCl_2$ and $(NH_4)_2CoCl_4$ in equimolar amounts. In the course of further decomposition, $(NH_4)_2CoCl_2$ breaks down in the temperature interval 350–400°C, to yield $CoCl_2$ and NH_4Cl (process 2). On further heating, the $CoCl_2$ produced in reactions (1) and (2) is oxidized to α-Co_3O_4 (process 3), which decomposes at 500–550°C to CoO (process 4). This is the final product of thermal decomposition of hexamminecobalt(III) chloride. The shapes of the thermoanalytical curves reveal that the oxidation of $CoCl_2$ takes the longest time.

For evaluation of the experimental results in order to calculate the kinetic parameters of these processes, the method developed by Kissinger [7] was used; this involves a graphical dependence of the following forms:

$$\ln(\Phi/T_m^2) = C - E/RT_m \quad (5)$$

where Φ, T_m, C, E and R are heating rate, temperature maximum peak on DTA, integration constant, activation energy and universal gas constant, respectively.

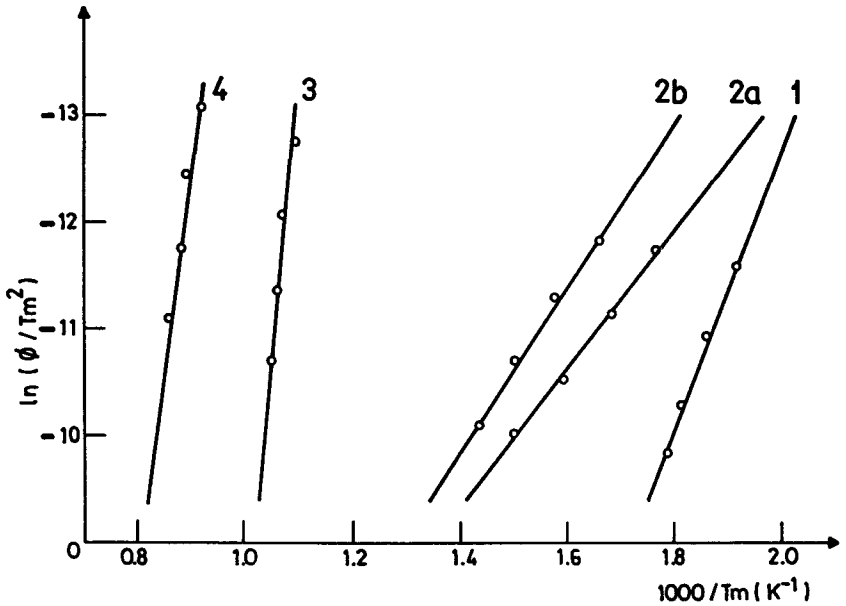

Fig. 2 Dependences $\ln(\Phi/T_m^2) = f(1/T_m)$ for the thermal decomposition process of $[Co(NH_3)_6]Cl_3$; 1 - process (1); 2a and 2b - process (2); 3 - process (3); 4 - process (4)

The graphical dependence $\ln(\Phi/T_m^2) = f(1/T_m)$ is shown in Fig. 2. The values of activation energy (E) and integration constant (C) presented in Table 2 were obtained on the basis of these results.

Table 2 Values for activation energy (E) and integration constant (C) for the processes of thermal decomposition of hexamminecobalt(III) chloride

Processes	E/kJ·mol^{-1}	C
(1)	132	$1.41 \cdot 10^8$
(2)→a	54	0.76
(2)→b	67	4.75
(3)	540	$1.94 \cdot 10^{25}$
(4)	186	$2.27 \cdot 10^3$

The obtained activation energy (E) and integration constant (C) values for the studied processes indicate that all processes take place in a kinetic region, or that the process temperature has a strong influence on the process rate. It is

obvious that process (2), the decomposition of $(NH_4)_2CoCl_4$, takes place in two stages (double DTA and DTG peak, Fig. 1). This is the reason for the determination of the kinetic parameters for the process in two parts: (2a) and (2b). The activation energy values (E) indicate an increased influence of diffusion resistance on the process development, possibly due to $CoCl_2$ formed on the surface of particles involved in the process (1). The rates of subsequent $CoCl_2$ oxidation and Co_3O_4 dissociation are limited only by the reaction rate at the reaction zone surface.

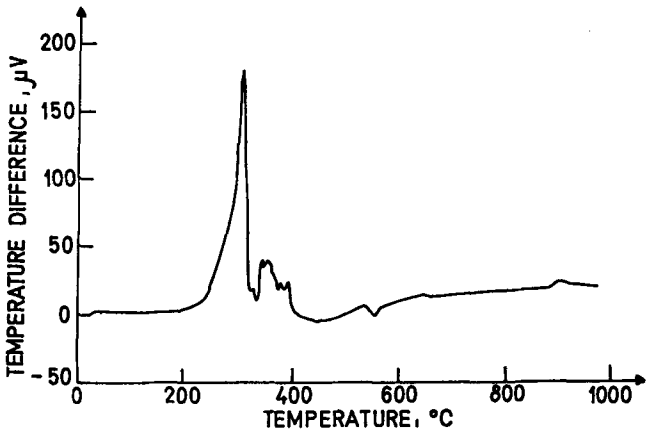

Fig. 3 DSC curve for $[Co(NH_3)_6]Cl_3$ in air atmosphere at the heating rate of 10 deg·min^{-1}

DSC measurements were used to determine the enthalpy of the studied processes, and the results are illustrated in Fig. 3. The calculated enthalpies of processes (1) to (4), and the time and temperature limits of the individual processes occurring in the course of hexamminecobalt(III) chloride thermal decomposition, are presented in Table 3.

Table 3 Values for enthalpies of the thermal decomposition process of $[Co(NH_3)_6]Cl_3$

Processes	Enthalpy/ J·g^{-1}	Limit/ °C	Limit/ min
(1)	6.652	215.1–328.3	10.8–16.1
(2)	2.638	348.2–416.0	16.9–20.1
(3)	–1.778	554.2–640.0	27.7–31.1
(4)	2.058	902.8–973.3	44.2–47.7

For the determination of C_p for the solid products formed in the course of thermal decomposition of $[Co(NH_3)_6]Cl_3$, heat flux DSC was best performed

according to the ratios method [8]. Sapphire discs are preferred for calibration. For processing of the results in order to calculate C_p for the products formed in the course of thermal decomposition of hexamminecobalt(III) chloride, a special software was used; the $C_p=f(T)$ dependence results are shown in Fig. 4.

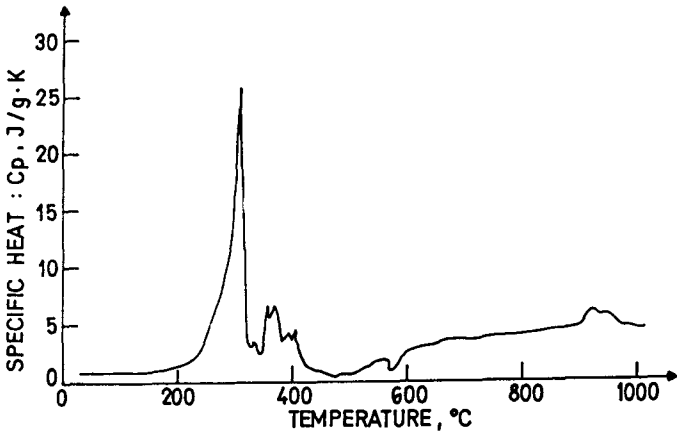

Fig. 4 Dependence $C_p=f(T)$ for solid products reactions of hexamminecobalt(III) chloride thermal decomposition

The DSC results supplement the results of simultaneous DTA-TG-DTG analysis, and present a more complete picture of the mechanism of hexamminecobalt(III) chloride thermal decomposition in relation to the earlier results.

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Zusammenfassung — Die Ergebnisse einer vergleichenden Thermoanalyse (TG-DTG-DTA-DSC) der thermischen Zersetzung von Hexamminkobalt(III)-chlorid in Luft wurden beschrieben. Weiterhin wurde die Kinetik und der Mechanismus der thermischen Zersetzung, die Enthalpie des Prozesses und die Änderung der spezifischen Wärmekapazität mit der Temperatur bestimmt.