

THERMAL DECOMPOSITION AND KINETIC DATA OF $\text{Cd}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$

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Abstract

The thermal dehydration and decomposition of $\text{Cd}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ were studied by means of DTA, TG, DSC and X-ray diffraction methods and the end products of the thermal decomposition were identified. The results of thermal analysis show that the compound is fused first, then it is dehydrated until $\text{Cd}(\text{BF}_4)_2 \cdot 3\text{H}_2\text{O}$ is obtained, which has not been described in the literature so far. The enthalpy of phase transition is $\Delta H_{\text{ph.tr.}} = 115.6 \text{ kJ mol}^{-1}$. Separation of the compound is difficult since it is highly hygroscopic. Then, dehydration and decomposition take place simultaneously until CdF_2 is obtained which is proved by X-ray diffraction. On further increasing the temperature, CdF_2 is oxidized to CdO and the characteristic curve assumes a linear character.

Based on TG data, kinetic analyses were carried out separately for both parts of the curve: first until formation of the trihydrate and then – until formation of CdF_2 . The formal kinetic parameters are as follows:

for the first phase: $E^* = 45.3 \text{ kJ mol}^{-1}$; rate equation $F = \alpha^{2/3}$; correlation coefficient 0.9858

for the second phase: $E^* = 230.1 \text{ kJ mol}^{-1}$; rate equation $F = (1 - \alpha)^{2/3} [1 - (1 - \alpha)^{1/3}]^{-1}$; correlation coefficient 0.9982.

Introduction

Information on the thermal behaviour of $\text{Cd}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ is rather scanty in the literature. It has been reported [1] that the substance is stable up to 60°C and decomposition begins with formation of BF_3 above this temperature. Kütek [2] has found a two-stage dehydration and reported on the existence of a dihydrate. The DTA and TG curves of $\text{Cd}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ taken at a relatively high heating rate ($10^\circ\text{C min}^{-1}$) were presented in [3] and formation of $\text{Cd}(\text{BF}_4)_2 \cdot 2\text{H}_2\text{O}$ was also proved.

The aim of the present study has been to supplement and extend information on the thermal decomposition of $\text{Cd}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, with the kinetic parameters of the dehydration process being calculated from TG data, and the enthalpy changes accompanying the most important phase transitions determined by DSC.

Experimental

The initial $\text{Cd}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ was obtained by the interaction of 50% HBF_4 ($\rho = 1.40 \text{ g cm}^{-3}$), and CaCO_3 , according to the method described in [1]. Cd^{2+} was determined complexometrically with EDTA and BF_4^- according to [4].

The DTA and TG curves were taken with a Paulik-Paulik-Erdey MOM OD-101 derivatograph at a heating rate of 5°C min^{-1} and a sample weight of 150 mg. The DSC curve was recorded on a Perkin-Elmer DSC-4 apparatus in the temperature range $25\text{--}350^\circ\text{C}$ at a heating rate of 5°C min^{-1} and a sample weight of 10 mg. The X-ray patterns of the intermediate stages were taken on a HZC 4C Zeiss apparatus (μK radiation with $\lambda = 1.542 \text{ \AA}$ in an interval 4 to $40^\circ \theta$).

Results and discussion

The TG, DTG and DTA curves of $\text{Cd}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ are shown in Fig. 1, and the DSC curve in Fig. 2. In Table 1 is presented the scheme of thermal dehydration and decomposition, while Table 2 shows the kinetic data calculated from TG data.

The dehydration process starts above 50°C (TG curve, Fig. 1), and at $T = 150^\circ\text{C}$ a clearly expressed delay can be observed, corresponding to a mass loss

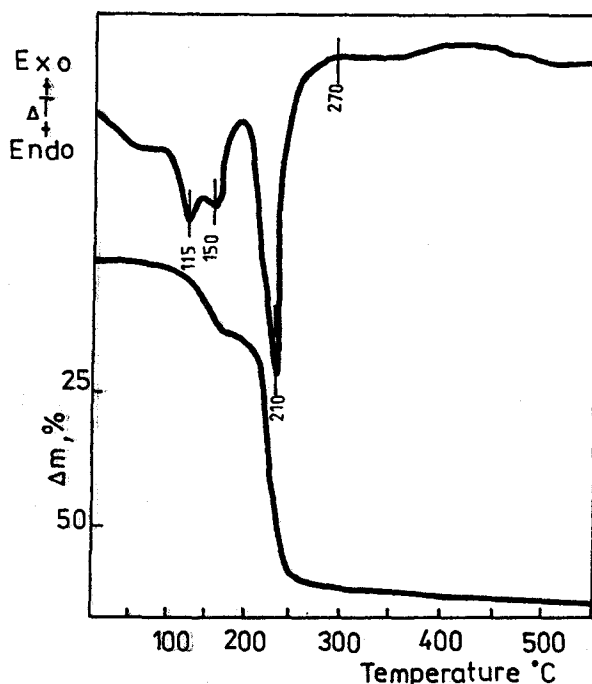


Fig. 1 DTA and TG curves of $\text{Cd}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$

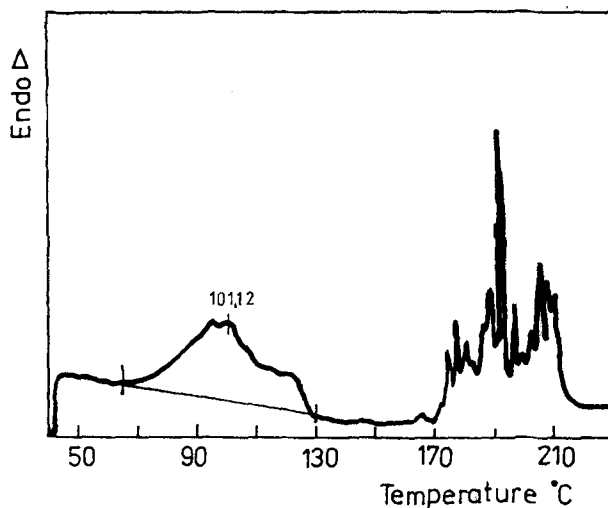


Fig. 2 DSC curve of Cd(BF₄)₂·6H₂O

of $\Delta m = 13.5\%$ ($\Delta m = 13.71\%$, calculated for the formation of Cd(BF₄)₂·3H₂O). Attempts to isolate the latter compound proved unsuccessful since it is highly hygroscopic. The trihydrate obtained in the course of the present study does not correspond to the dihydrate described in [2, 3]. This difference may be due to the different conditions, under which the present experiment was conducted, namely: the sample mass and the heating rate (5°C min^{-1}) were both lower by a factor of 2. The further course of the TG curve reveals a continuous reduction of the sample mass involving evolution of the remaining hydrate water and decomposition of the anhydrous product. However, the corresponding DTA curve indicates both stages of dehydration by two well-defined endothermic peaks at 115 and 150°C (Fig. 1), and the decomposition of the anhydrous salt by an endothermic peak at 210°C.

It is interesting to compare the TG and DTA curves obtained simultaneously with the DSC curve of the compound. Two endothermal effects can be observed in the DSC curve. The first of them is assigned to the partial dehydration (Table 1, row 1). The $\Delta H_{\text{ph.t.}}$ value is $115.6 \text{ kJ mol}^{-1}$ and it is close to that calculated for evaporation of three molecules crystallization water. This fact is another proof for the formation of intermediate Cd(BF₄)₂·3H₂O. The second endothermal effect is related both with the last step of dehydration process and with the decomposition of the compound (Table 1, row 2). The enthalpy change of the latter effect cannot be accurately calculated due to the complex character of the registered peak (Fig. 2).

The total mass loss of the sample after decomposition of Cd(BF₄)₂·3H₂O to CdF₂ ($T = 285^\circ\text{C}$) is 62%, the theoretical value being 61.8%. On further increasing the temperature the TG curve reveals only an insignificant mass loss.

Table 1 DTA, TG and DSC data for $\text{Cd}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$

No.	Phase transition	DTA and TG data				DSC data			
		$T_{\text{max}}/^\circ\text{C}$		$\Delta m/\%$		$T/^\circ\text{C}$		$\Delta H_{\text{ph.t.}}$	
		calc.	exp.	calc.	exp.	T_{onset}	T_{max}	cal g^{-1}	kJ mol^{-1}
1	$\text{Cd}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{Cd}(\text{BF}_4)_2 \cdot 3\text{H}_2\text{O}$	115	13.71	13.50	82.42	101.12	70.18	115.6	
2	$\text{Cd}(\text{BF}_4)_2 \cdot 3\text{H}_2\text{O} \rightarrow \text{CdF}_2 \cdot 2\text{BF}_3 + 3\text{H}_2\text{O}$	150.21	61.82	62	170	191.78	—	—	
3	CdF_2 residue	over 250				205.11			
4	$\text{CdF}_2 \rightarrow \text{CdO}$	over 300							

Table 2 Kinetic data for the process of decomposition of $\text{Cd}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$

Process stages	Temperature interval	Kinetic equation	$E^*/\text{kJ mol}^{-1}$	R
$\text{Cd}(\text{BF}_4)_2 \cdot n\text{H}_2\text{O}$				
$6\text{H}_2\text{O} \rightarrow 3\text{H}_2\text{O}$	60–150°C	$F = \alpha^{2/3}$	45.3	0.9858
$3\text{H}_2\text{O} \rightarrow \text{CdF}_2$	160–240°C	$F = (1 - \alpha)^{2/3} [1 - (1 - \alpha)^{1/3}]^{-1}$	230.1	0.9982

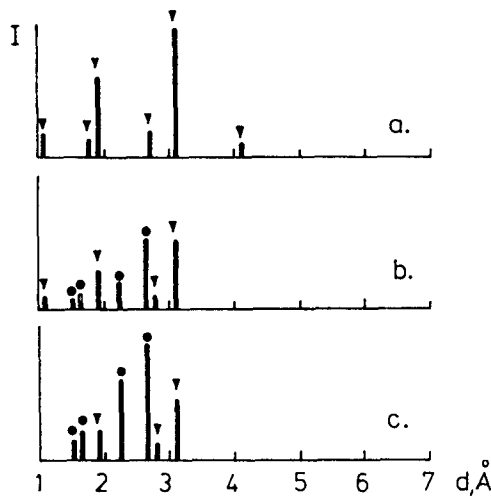


Fig. 3 Interplanar distance at (a) $T=300^{\circ}\text{C}$; (b) $T=400^{\circ}\text{C}$; (c) $T=500^{\circ}\text{C}$; \blacktriangledown – CdF_2 ; \bullet – CdO

The corresponding DTA curve exhibits a wide, poorly formed endothermic effect starting at 300°C . The TG and DTA curves above this temperature indicate the oxidation of CdF_2 to CdO , as proved by the results of analysis for Cd^{2+} of the products of the reaction stopped at different temperatures, as well as their X-ray patterns, showing reflections for both CdF_2 and CdO . The results (Fig. 3) show that the proportion of CdO increases with time and temperature increase.

Based on TG data, the kinetics of the dehydration process ($6\text{H}_2\text{O}-3\text{H}_2\text{O}$) and of the dehydration and decomposition process ($3\text{H}_2\text{O}-\text{CdF}_2$) was characterized in the isothermal mode. A computer program was used, including 25 kinetic equations described in the literature, for which – upon comparison with experimental data from the TG curve – the values of E^* , the standard deviation (for the interval) and the correlation coefficient were obtained [5]. The data are shown in Table 2.

The kinetic data show that during the first stage the dehydration process takes place in the diffusion area, while during the second stage (which also includes the decomposition process) the process takes place within the kinetic area.

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