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THERMOCHEMISTRY OF THE DECOMPOSITION OF SOME COBALT COMPOUNDS

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Abstract

Differential scanning calorimetry (DSC) was used to determine the molar enthalpies of dehydration and decomposition of $CoC_2O_4·2H_2O$, $Co(HCOO)_2·2H_2O$ and $[Co(NH_3)_6]_2(C_2O_4)_3·4H_2O$. The first stage of dissociation of each compound is a single-step dehydration both in air and argon atmospheres. The next stages are decomposition processes influenced by experimental parameters. The enthalpies of dehydration and decomposition vary from compound to compound in each atmosphere. The obtained data have been related to the macromechanisms proposed for the thermal decomposition and the parallel-consecutive decomposition-oxidation processes.

Keywords: cobalt oxysalts, DSC, enthalpy of decomposition, enthalpy of dehydration, thermal decomposition

Introduction

This work is a part of our studies [1–5] of the thermal decomposition of some transition metal salts with some carboxylic acids. The importance of this subject arises from the possibility of these salts being used for preparation of metal powders, powdered alloys and oxide catalysts [6–11]. In the accessible literature there are no data available concerning the enthalpy values of the thermal decomposition of $[Co(NH)_3]_6(C_2O_4)_3.4H_2O$ (HACOT) and $Co(HCOO)_2·2H_2O$ (CFD). However, there are some papers with the kinetics and enthalpy data of dehydration and decomposition of some transition metal oxalates [6, 8, 10, 12–14]. Dollimore [10–12] extensively reviewed the thermal decomposition and dehydration of some metal oxalates along with their useful analytical applications. The literature data referring to the thermal decomposition of $CoC_2O_4·2H_2O$ (COD) diverge considerably [1, 6, 10–15]. Little information is available on CFD thermal decomposition [12, 15, 17–19]. The influence of an ambient gas atmosphere on the process and composition of final products of thermal decomposition of the studied compounds (COD, CFD and HACOT) was investigated by the authors earlier [1–3].

The aim of the present work is to measure the heat values of the dehydration and decomposition reactions of the compounds under investigation. The attempt to relate the thermodynamic data to the suggested macromechanisms of the thermal decomposition processes was made.

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Experimental

The samples of the salts (COD, CFD and HACOT) used throughout the present work were from the same preparation of reactants as studied previously [1–3].

Enthalpies of the reactions were measured using a SETARAM DSC 121 differential scanning calorimeter. Decomposition reactions in dynamic argon and static air were studied using open quartz ampoules (~7 mm in the length and ~6 mm in diameter) filled with the samples. During the standard measurements an ampoule with an opening of ~1.5 mm in diameter was used. Additional measurements in static air atmosphere using an ampoule with an opening of ~6 mm were carried out. Different heating rates, β, within the range from 10 to 1°C $\min^{-1}$ were applied. The mass of the samples was a few tens of milligrams.

Results and discussion

The DSC curves for COD and CFD heated at 5°C $\min^{-1}$ in argon (Figs 1 and 2) show the occurrence of two distinct endothermic processes (the extrapolated onset temperatures, T_e, are presented in Table 1) identified previously as dehydration and following decomposition of anhydrous salts [1]. On the DSC trace of HACOT in ar-

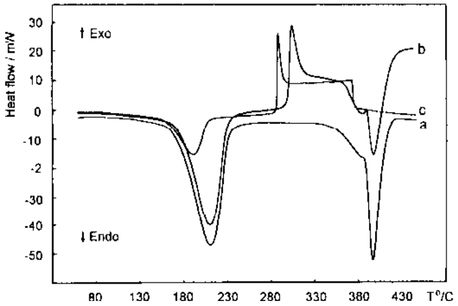

Fig. 1 DSC curves of $CoC_2O_4 \cdot 2H_2O$ thermal decomposition: a) in argon (β=5°C $\min^{-1}$); b) in air (β=5°C $\min^{-1}$); c) in air (β=2°C $\min^{-1}$)

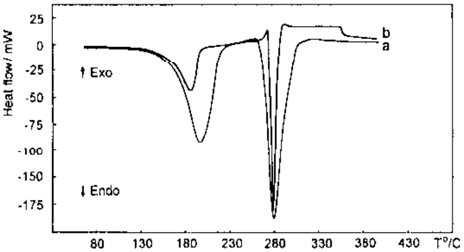

Fig. 2 DSC curves of $Co(HCOO)_2 \cdot H_2O$ thermal decomposition: a) in argon (β=5°C $\min^{-1}$); b) in air (β=2°C $\min^{-1}$)

gon (β=1°C min^{-1}) four endothermic effects (Fig. 3) can be observed. The first one is the single-staged dehydration, the subsequent effects were connected with some

Table 1 Experimentally evaluated molar enthalpies (from DSC data) of the dehydration and decomposition reactions

Compound	Procedural parameters			T_e/ °C	ΔH_m^*/ kJ mol^{-1}	Type of reaction
	atm.	β/ °C min^{-1}	Mass/ mg			
$CoC_2O_4 \cdot 2H_2O$	argon	5	34.92	173.3	107.3	dehyd.
				368.2	65.57	decomp.
	air	5	35.19	178.6	113.2	dehyd.
				300.4	–37.98	decomp.+oxid.
				385.7	58.56	decomp.+oxid.
	air[**]	5	30.36	175.8	114.4	dehyd.
				298.6	–243.6	decomp.+oxid.
	air	2	20.03	159.5	119.8	dehyd.
				286.8	–260.7	decomp.+oxid.
$Co(HCOO)_2 \cdot 2H_2O$	argon	5	57.35	167.8	134.3	dehyd.
				267.7	130.0	decomp.
	air	5	88.96	176.8	134.7	dehyd.
				270.2	–0.533	decomp.+oxid.
				277.7	132.2	decomp.+oxid.
				334.7	–0.716	decomp.+oxid.
	air	2	64.05	165.7	127.7	dehyd.
				266.9	–1.911	decomp.+oxid.
				271.9	132.9	decomp.+oxid.
				289.4	–1.189	decomp.+oxid.
$[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4H_2O$	argon	1	56.00	132.6	190.9	dehyd.
				183.4	459.5	decomp.
				253.3	9.546	decomp.
				297.0	65.70	decomp.
	air	1	69.74	160.7	174.3	dehyd.
				186.0	424.8	decomp.
				216.9	16.52	decomp.
				231.6	–28.51	decomp.+oxid.

[*]Error limits ±5 %

[**]The shape of the sample holder with better air access (see Experimental)

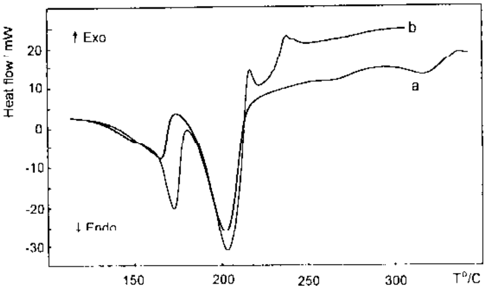

Fig. 3 DSC curves of $[Co(NH_3)_6]_2(C_2O_4)_3{\cdot}4H_2O$ thermal decomposition: a) in argon (β=1°C min^{-1}); b) in air (β=1°C min^{-1})

decomposition reactions as it was found earlier [2–4]. As it can be seen the first two heat effects are not quite separated. Because of that the evaluated values of enthalpy could be underestimated.

The thermal decomposition of the studied salts in air is accompanied by endo- and exothermic effects (Figs 1–3). The magnitude of the exothermic effects depends on a heating rate and an air access, as it is shown for COD (Table 1). In the case of CFD and HACOT the comparison of DSC (Figs 2 and 3) and DTA curves presented previously [1, 4] confirms the conclusion mentioned above. The first endothermic peak observed in the DSC traces in air of all the examined salts is ascribed to the single step process of dehydration like it is in argon. The following sequence of consecutive endo- and exothermic effects present in the DSC curves is the result of the decomposition of anhydrous salts and the oxidation of the intermediates.

In the case of an open air access to the heated oxalate as well, as in the case of a low heating rate (β=2°C min^{-1}) only two effects are noticeable in the DSC (and DTA [1, 10]) curves. The first one is endothermic (dehydration) and the second one is exothermic. The latter, probably connected with oxidation of the intermediates, overlaps the endothermic effect connected with decomposition of the anhydrous salt.

The extrapolated onset temperatures, T_e, and the determined molar enthalpies of the dehydration, and that of the decomposition as well as the total decomposition and oxidation enthalpies, ΔH_m, are listed in Table 1. For each of the investigated compounds the molar dehydration enthalpy values, $\Delta_{deh}H_m$, measured in air as well as in argon atmosphere, are close. The calculated $\Delta_{deh}H_m$ values for the oxalate correlate well with the literature data [6, 13]. For the other compounds (CFD and HACOT) no data have been found. On the other hand, the dehydration and decomposition enthalpies measured in both atmospheres are different for different compounds. The determined enthalpy of the oxalate decomposition in argon is clearly lower than the one by Coetzee *et al.* [6] (i.e. 97.5 kJ mol^{-1}) and significantly higher than the one by Nagase *et al.* [13] (36.0 kJ mol^{-1}).

The determined values of enthalpy of the second and the third endothermic effect of HACOT decomposition in argon and air (limited access) are suggested to be enthalpies of the following reactions:

$$3[\mathrm{Co(NH_3)_6}]_2(\mathrm{C_2O_4})_3 \rightarrow 6(\mathrm{CoC_2O_4{\cdot}NH_3})+\mathrm{N_2}+28\mathrm{NH_3}+3\mathrm{H_2O}+3\mathrm{CO}+3\mathrm{CO_2} \quad (1)$$

$$\mathrm{CoC_2O_4{\cdot}NH_3} \rightarrow \mathrm{CoC_2O_4}+\mathrm{NH_3} \quad (2)$$

The reactions were assumed earlier [2–4]. The verification of the above reactions is not possible currently due to the lack of the appropriate thermodynamic data. The last endotherm in argon and the exotherm in air are ascribed to the decomposition or to the decomposition and oxidation of the intermediate, respectively. It is assumed that the intermediate can be CoC_2O_4 [2, 4].

Previously, the final product of the decomposition of all the studied compounds was revealed to be a mixture of Co and CoO in argon, but Co_3O_4 in air.

The molar enthalpy values calculated for the thermodynamically probable ($\Delta G<0$) reactions that can occur during decomposition of the examined compounds are listed in Table 2. Taking into account all the available values of molar enthalpy of formation, $\Delta_f H^0_m$ (CoC_2O_4) [6, 20, 21], $\Delta_r H_{m(calc)}$ values for reactions No.1–10 listed in Table 2 were calculated. The majorities of the $\Delta_r H_{m(calc)}(CoC_2O_4)$ values fall into the ranges given in Table 2. Comparing the measured enthalpy values ($\Delta_r H_{m(exp)}$; Table 1) and the calculated ones ($\Delta_r H_{m(calc)}$; Table 2) it can be concluded that the decomposition of CoC_2O_4 in argon can pass as well through the parallel reactions No. 1 and 2 as through the parallel-consecutive reactions No. 2 and 3.

The values of $\Delta_r H_{m(exp)}$ of the exothermic process of CoC_2O_4 decomposition in air ($\beta=2$ or $\beta=5$°C min^{-1} with better air access (Table 1)) are close to the value $-(265\pm5)$ kJ mol^{-1} given in [6] for CoC_2O_4 decomposition in oxygen. These values fall into the range of $\Delta_r H_{m(calc)}$ calculated for reaction No. 5 (Table 2).

Table 2 The molar enthalpy values calculated for some thermodynamically probable ($\Delta G<0$) reactions that can occur during decomposition of the examined compounds (T=600 K) [22] and [6, 20, 21]

No.	Reaction	$\Delta_r H_m$/kJ mol^{-1}
1	$CoC_2O_4 \rightarrow Co+2CO_2$	62–98*
2	$CoC_2O_4 \rightarrow CoO+CO+CO_2$	81–130*
3	$CoO+CO \rightarrow Co+CO_2$	−49.53
4	$Co+CO \rightarrow CoO+C$	−124.4
5	$CoC_2O_4+2/3O_2 \rightarrow 1/3Co_3O_4+2CO_2$	(−240.6)–(−204.7)*
6	$Co(HCOO)_2 \rightarrow CoO+H_2O+2CO$	173.9±6.7**
7	$Co(HCOO)_2 \rightarrow CoO+CO+CO_2+H_2$	135.0±6.7**
8	$Co(HCOO)_2 \rightarrow Co+2CO_2+H_2$	86.0±6.7**
9	$Co(HCOO)_2 \rightarrow Co+H_2O+CO+CO_2$	124.9±6.7**
10	$CoO+H_2 \rightarrow Co+H_2O$	−10.17

*The assumed range of $\Delta_f H^0_m$ (CoC_2O_4) equals 850–886 kJ mol^{-1} [6, 20, 21]

**The assumed value of $\Delta_f H^0_m$ ($Co(HCOO)_2$) = 873.6±6.7 kJ mol^{-1} [20]

The value of $\Delta_r H_{m(calc)}$ for $Co(HCOO)_2$ decomposition was calculated using the only available $\Delta_f H^o_m$ value [20]. The comparison of the values of $\Delta_r H_{m(exp)}$(Table 1) and $\Delta_r H_{m(calc)}$(Table 2) points out the possibility of reactions No. 7 and 9. However, the quantitative composition of the gas products published in [17] is out of agreement with the above assumption. Such combination of reactions No. 7 and 3 that 20% of CoO produced by reaction No. 7 is reduced in reaction No. 3, leads to the quantitative composition of gas products similar to that in [17]. Then the overall heat of the decomposition process equals ~125 kJ mol^{-1}. The same value can be obtained on the assumption that 80 % of the reactant decomposes through reactions No. 7 and the rest through reaction No. 8.

Conclusions

1 – Dehydration of all the compounds under investigation is a single step process.

2 – For each of the studied compounds an influence of an ambient atmosphere on the decomposition process of an anhydrous salt has been found.

3 – The thermal decomposition of each of those compounds is a complex process influenced by procedural parameters.

4 – The presented data do not allow to choose the proper sequence of chemical reactions of the decomposition of the examined compounds undoubtedly.

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