Journal of Thermal Analysis, Vol. 54 (1998) 115-123

THERMAL ANALYSIS OF COBALT(II) SALTS WITH SOME CARBOXYLIC ACIDS

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Abstract

The thermal analysis of $CoC_2O_4 \cdot 2H_2O$, $Co(HCOO)_2 \cdot 2H_2O$ and $Co(CH_3COO)_2 \cdot 4H_2O$ was carried out with simultaneous TG-DTG-DTA measurements under non-isothermal conditions in air and argon atmospheres. The intermediates and the end products of decomposition were characterised by X-ray diffraction and IR and UV-VIS spectroscopy. The decomposition of the studied compounds occur in several stages. The first stage of dissociation of each compound is dehydration both in air and argon. The next stages differ in air and argon. The final product of the decomposition of each compound in air is Co_3O_4. In argon it is a mixture of Co and CoO for cobalt(II) oxalate and cobalt(II) formate but CoO for cobalt(II) acetate.

Keywords: cobalt(II) salts decomposition, thermal analysis

Introduction

The importance of thermal behaviour studies of transition metal oxalates, formates and acetates arises from the possibility of their use for preparation of metal powders or metal and metal oxide catalysts [1]. The literature data referring to thermal decomposition of $CoC_2O_4 \cdot 2H_2O$ diverge considerable on the temperature range of dehydration and decomposition processes and first of all on the final products of its decomposition in argon e.g. [2–10]. There is an agreement that the end residue formed in air is Co_3O_4 [2–11]. There have been wide variations in the interest shown in the transition metal formates. Nickel and copper formates have been the subject of detailed investigations. Little information is available on cobalt formate [3, 12–15]. There have been relatively few studies of decomposition of metal acetates [3, 16, 17].

The aim of the present work is to determine the influence of an ambient gas atmosphere and the kind of anion on the composition of final products of dissociation of the studied compounds i.e. $CoC_2O_4 \cdot 2H_2O$, $Co(HCOO)_2 \cdot 2H_2O$ and $Co(CH_3COO)_2 \cdot 4H_2O$. It is also to find some similarities and/or differences characterising the course of the thermal decomposition of the compounds under investigation.

1418–2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Experimental

Materials

The compounds i.e. $CoC_2O_4 \cdot 2H_2O$, $Co(HCOO)_2 \cdot 2H_2O$ and $Co(CH_3COO)_2 \cdot 4H_2O$ were synthesised according to the reactions (1–3):

$$CoCl_2+H_2C_2O_4 \rightarrow CoC_2O_4+2HCl \qquad (1)$$

$$CoCO_3+2HCOOH \rightarrow Co(HCOO)_2+CO_2+H_2O \qquad (2)$$

$$CoCO_3+2CH_3COOH \rightarrow Co(CH_3COO)_2+CO_2+H_2O \qquad (3)$$

All the chemicals used for the synthesis processes were of p.a. grade from POCh – Gliwice.

The purity of the obtained compounds were tested by elemental analysis, chemical analysis and X-ray powder diffraction methods. The results of the analysis of $CoC_2O_4 \cdot 2H_2O$ were Co, 32.6% found, 32.2% calc.; H, 2.35% found, 2.20% calc.; C, 13.1% found, 13.1% calc. For $Co(HCOO)_2 \cdot 2H_2O$ they were Co, 32.9% found, 31.9% calc.; H, 3.41% found, 3.27% calc.; C, 12.6% found, 13.0% calc. For $Co(CH_3COO)_2 \cdot 4H_2O$ they were: Co, 24.3% found, 23.6% calc.; H, 4.53% found, 5.68% calc.; C, 21.0% found, 19.3% calc.

Methods

Simultaneous TG-DTG-DTA curves under non-isothermal conditions were obtained with a Derivatograph C (MOM, Budapest) in static air and flowing argon atmospheres ($\sim 4\ dm^3\ h^{-1}$) between 293 and 773 K with heating rates $\beta=10$, 5 and 2 K min^{-1} in air and $\beta=5$ K min^{-1} in argon. The sample mass was ~100 mg. Crucibles of alumina were used both for the specimen and for the reference material, which was calcined alumina.

X-ray diffraction patterns (XRD) of the substrates, intermediate and final residues were obtained on a Philips 1680 X Pert diffractometer with a CuK_α radiation lamp.

Reflectance spectra of the solids were recorded in the range 800–200 nm on a Hitachi M 356 spectrophotometer. The reference material was magnesium oxide.

Infrared (IR) and far infrared (FTIR) spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer between 4000–400 cm^{-1} and in the region 675–30 cm^{-1}. Samples were prepared in the form of KBr discs (for the former) or dispersed in Nujol (for the latter).

Procedure

Each of the intermediates of the thermal decomposition studied compounds was isolated by stopping the reactions and cooling the residue to room temperature immediately as the appropriate mass loss was reached. The intermediates of $CoC_2O_4{\cdot}2H_2O$ decomposition (β=10 K min^{-1} air) were taken out at the mass losses of 18.4% (A), 30.2% (B) and 59.6% (C). The intermediates of $Co(HCOO)_2{\cdot}2H_2O$ decomposition (β=2 K min^{-1}; air) were taken out at the mass losses of 19.0% (A), and 58.6% (B). The intermediates of $Co(CH_3COO)_2{\cdot}4H_2O$ decomposition (β=2 K min^{-1}; air) were taken out at the mass losses of 21.5% (A) and 60.9% (B). The end products of decomposition in argon were flooded with paraffin oil to protect oxidising.

Results and discussion

Thermal analysis

The profiles of TG-DTG-DTA curves obtained for the thermal decomposition of $CoC_2O_4{\cdot}2H_2O$ in air and argon atmospheres are shown in Fig. 1. The representative thermoanalytical data obtained at heating rate β=5 K min^{-1} are listed in Table 1. It was revealed that number of observed stages of $CoC_2O_4{\cdot}2H_2O$ depends on heating rate. The decomposition (β=5 K min^{-1}) of cobalt(II) oxalate and cobalt(II) formate occurs in two or three stages as it is shown in Table 1. In air the third stage is oxidation of CoO to Co_3O_4. The dissociation of $Co(CH_3COO)_2{\cdot}4H_2O$ is more complicated. The three stages in argon and four in air were observed (Table 1). All the decomposition reactions of the examined compounds occurrring in argon are endothermic, in air both endo- and exothermic. For the first stage of

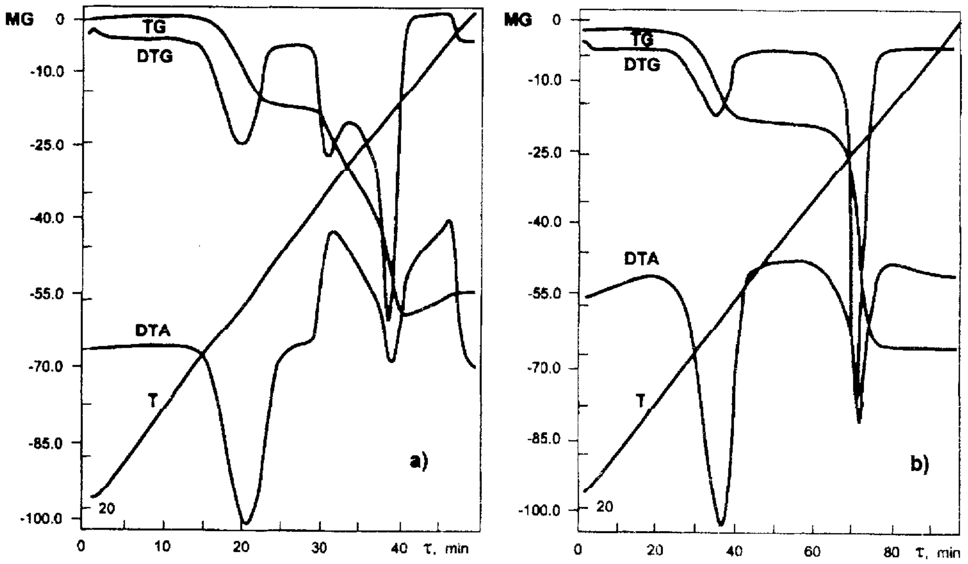


Fig. 1 Thermoanalytical curves of $CoC_2O_4{\cdot}2H_2O$, decomposition: a) in air (β=10 K min^{-1}), b) in argon (β=5 K min^{-1})

Table 1 Thermoanalytical results (TG-DTG-DTA) on the examined compounds decomposition in air and argon; β=5 K min^{-1}; m=100 mg

Compound	Stage	T_{range}/	DTG_{max}/	DTA_{peak}/	Mass loss/%		Composition of residue	Atm.
			K		obs.	calc.		
$CoC_2O_4{\cdot}2H_2O$	I	378-536	475	477endo	18.3	19.7	CoC_2O_4	air
	II	541-660	562	568exo	36.8	36.4	Co_3O_4	air
	I	357-550	472	474endo	19.1	19.7	CoC_2O_4	argon
	II	567-713	643	645endo	46.4	43.7	Co+CoO (50%)	argon
$Co(HCOO)_2{\cdot}2H_2O$	I	387-494	451	453endo	19.1	19.5	$Co(HCOO)_2$	air
	II	494-584	550	547exo	40.2	40.0	CoO	air
				551endo				
	III	584-636	612	580exo	+3.6	+2.9	Co_3O_4	air
				614exo				
	I	377-494	450	453endo	19.3	19.5	$Co(HCOO)_2$	argon
	II	495-638	536	537endo	41.6	44.3	Co+CoO (50%)	argon
$Co(CH_3COO)_2{\cdot}4H_2O$	I	343-486	397	396endo	22.7	23.1	$Co_3(CH_3COO)_5OH+4Co(CH_3COO)_2{\cdot}2H_2O$	air
	II	486-532	518	518endo	6.5	5.8	$Co_3(CH_3COO)_5OH+Co(OH)_2+Co(CH_3COCH_2COO)_2$	air
	III	532-648	573	543endo	32.1	31.3	$3CoO+Co_3O_4+Co_3O(CH_3COO)_4$*	air
				576endo				
			630	621exo				
	IV	648-699	667	665exo	+1.42	+0.7	$2Co_3O_4+Co_3O(CH_3COO)_4$*	air
	I	338-485	398	399endo	22.6	23.1	$Co_3(CH_3COO)_5OH+4Co(CH_3COO)_2{\cdot}2H_2O$	argon
	II	485-548	517	529endo	8.2	8.3	$1/2Co_3(CH_3COO)_5OH+Co(OH)_2+Co(CH_3COCH_2COO)_2$	argon
	III	548-644	584	584endo	32.4	31.3	CoO+3/2C	argon
			610	611endo				

*Tentative formula

dissociation of each compound, the observed thermoanalytical parameters in air and argon (Table 1) are nearly the same. It may be assumed that the transitions occurring are independent of the gas atmosphere. However, for the second stages for all compounds and third stage for cobalt(II) acetate the observed temperature parameters and mass losses are different in air and argon.

XRD investigation

Investigations by XRD analysis allowed to identify the end products and some of the intermediates of the decomposition of the tested compounds in air and argon. The results are gathered in Table 2. X-ray patterns of the final products of dissociation in argon are shown in Fig. 2.

Table 2 Intermediate and final products of the thermal decomposition of the examined cobalt(II) compounds identified based on XRD results

Compound	Atm.	β/K min^{-1}	T_f/K	Residue
$CoC_2O_4{\cdot}2H_2O$	air	10	563	$CoC_2O_4^{A,B}$
			690	CoO^C
			760	$Co_3O_4^R$
		5	660	$Co_3O_4^R$
		2	645	$Co_3O_4^R$
	argon	5	715	$Co+CoO^R$
$Co(HCOO)_2{\cdot}2H_2O$	air	10	735	$Co_3O_4^R$
		5	635	$Co_3O_4^R$
		2	560	CoO^B
			575	$Co_3O_4^R$
	argon	5	640	$Co+CoO^R$
$Co(CH_3COO)_2{\cdot}4H_2O$	air	10	675	$Co_3O_4+X^R$
		5	700	$Co_3O_4+X^R$
		2	450	$Co_3(CH_3COO)_5OH^A$
			585	$CoO+Co_3O_4+X^B$
			605	$Co_3O_4+X^R$
	argon	5	645	$CoO+1.5C^R$

^{A}intermediate A; ^{B}intermediate B; ^{C}intermediate C; ^{R}final product;
X: unidentified species with acetate group

On the whole the intermediates of decomposition of all the studied compounds were either poorly crystallised or even completely amorphous. It caused their identification to be difficult. However, it was possible to identify the inter-

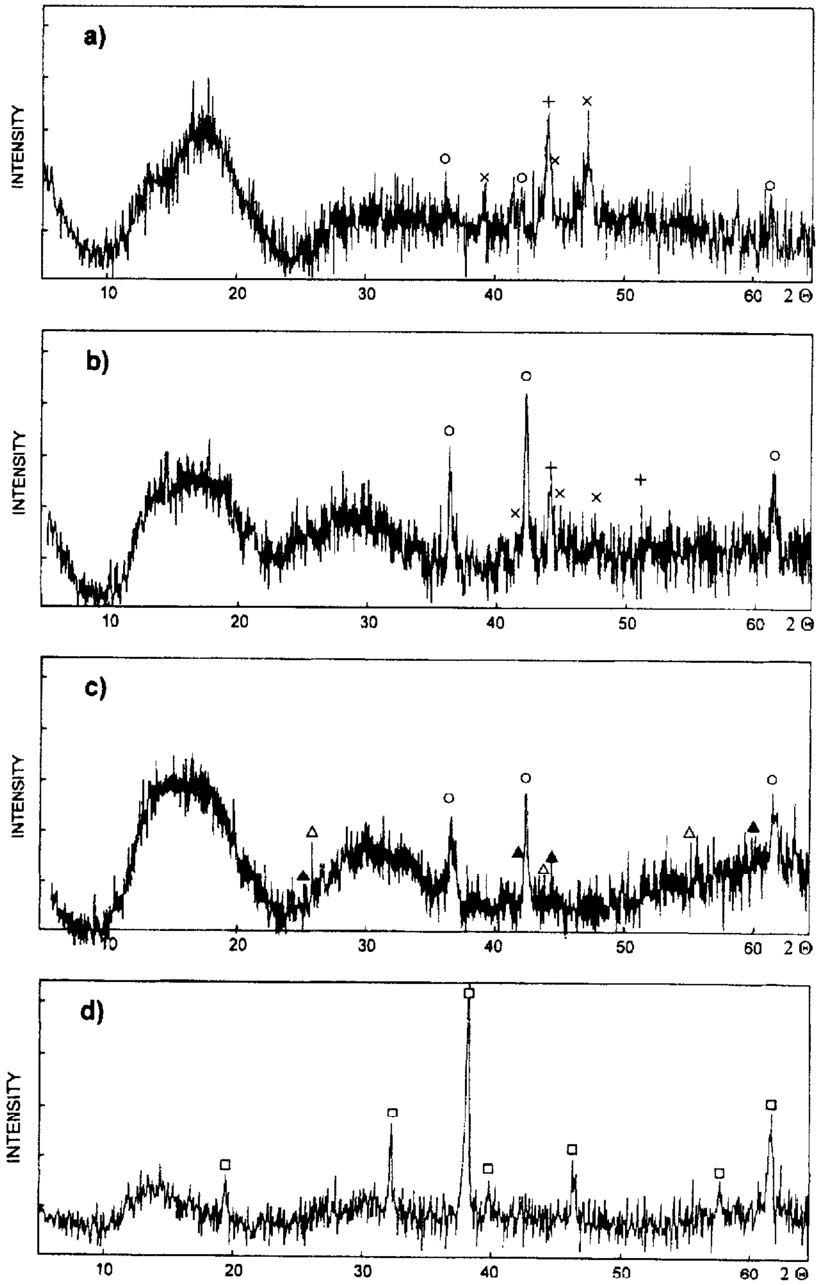


Fig. 2 XRD diffractograms of the final products of decomposition: a) $CoC_2O_4 \cdot 2H_2O$ in argon, b) $Co(HCOO)_2 \cdot 2H_2O$ in argon, c) $Co(CH_3COO)_2 \cdot 4H_2O$ in argon, d) $CoC_2O_4 \cdot 2H_2O$ in air o – CoO; △ – C; + – β-Co; ▲ – C; × – α-Co; □ – Co_3O_4

mediates A of $CoC_2O_4 \cdot 2H_2O$ and $Co(CH_3COO)_2 \cdot 4H_2O$ decomposition and the intermediates B of all the studied compounds dissociation (Table 2).

Infrared spectroscopy

Analysis of the IR-FTIR spectra (substrates, intermediates and final residues) revealed that the intermediates A of $CoC_2O_4 \cdot 2H_2O$ and $Co(HCOO)_2 \cdot 2H_2O$ decomposition in air were anhydrous compounds. The spectra of a substrate and the intermediate A for each couple are nearly the same but the spectra of intermediates A exhibit only the lack of an absorption band ~580 cm^{-1} typical for crystallization H_2O. The spectrum of the intermediate A of $Co(CH_3COO)_2 \cdot 4H_2O$ decomposition shows, apart from the typical bands of the substrate, an additional band ~3638 cm^{-1} characteristic of stretching frequencies in OH group [18]. In the final products spectra of all studied compounds there were observed frequencies of Co_3O_4 [19] i.e. ~665 cm^{-1}, ~560 cm^{-1} and ~390 cm^{-1}. The spectrum of cobalt(II) acetate residue apart from those mentioned above shows two very weak bands ~1384 cm^{-1} and ~837 cm^{-1} present in the substrate.

Reflectance spectroscopy

The diffuse reflectance spectra of all studied compounds have a broad band with the maximum at about 510–535 nm characteristic for $^4T_{1g}(F)$—$^4T_{1g}(P)$ transition in high spin (d^7) species of Co(II) ion in octahedral environment [20]. Spectra of the intermediates A are very similar to those of their substrates except some relatively small shifts of the absorption bands. Thus the Co(II) ion of the intermediates A is also in an approximately octahedral arrangement.

Decomposition

The results proved the first stage of decomposition of all the compounds under investigation in air and argon was dehydration. In case of $CoC_2O_4 \cdot 2H_2O$ and $Co(HCOO)_2 \cdot 2H_2O$ the dehydration runs in one stage and the products are anhydrous salts. In case of $Co(CH_3COO)_2 \cdot 4H_2O$ the dehydration in air and argon probably runs as a set of parallelly-consecutive reactions according to Eqs (4–6):

$$Co(CH_3COO)_2 \cdot 4H_2O \rightarrow Co(CH_3COO)_2 \cdot 2H_2O + 2H_2O \qquad (4)$$

$$3Co(CH_3COO)_2 \cdot 2H_2O \rightarrow Co_3(CH_3COO)_5OH + H_2O + CH_3COOH \qquad (5)$$

$$2Co(CH_3COO)_2 \cdot 2H_2O \rightarrow Co(CH_3COCH_2COO)_2 + Co(OH)_2 + 2H_2O \qquad (6)$$

Cobalt acetate hydroxide is the intermediate A identified by XRD. Cobalt acetoacetate is adopted from literature data [16].

In the next stage of decomposition in argon the products of reactions (5) and (6) destroyed e.g. according to the reactions (7–10):

$$Co_3(CH_3COO)_5OH \rightarrow 3CoO+8H_2O+10C \tag{7}$$

$$Co_3(CH_3COO)_5OH \rightarrow 3CoO+8H_2+8CO+2C \tag{8}$$

$$Co(CH_3COCH_2COO)_2 \rightarrow CoO+2CH_3CHO+H_2+3CO+C \tag{9}$$

$$Co(CH_3COCH_2COO)_2 \rightarrow CoO+2CH_3CHO+H_2O+2CO+2C \tag{10}$$

In air the products of reactions (5) and (6) decompose and oxidise at the same time successively to CoO and Co_3O_4 may be as follows:

$$Co_3(CH_3COO)_5OH+10O_2 \rightarrow 3CoO+10CO_2+8H_2O \tag{11}$$

$$Co_3(CH_3COO)_5OH+2O_2 \rightarrow Co_3O(CH_3COO)_4+2H_2O+2CO_2 \tag{12}$$

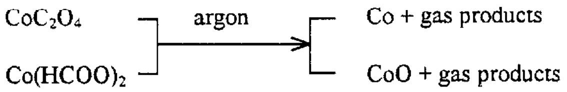
$$2Co_3(CH_3COO)_5OH+21O_2 \rightarrow 2Co_3O_4+16H_2O+20CO_2 \tag{13}$$

$$Co(CH_3COCH_2COO)_2+3O_2 \rightarrow CoO+2CH_3CHO+H_2O+4CO_2 \tag{14}$$

To construct the above reaction equations the literature data [16] on gas and volatile products of $Co(CH_3COO)_2{\cdot}4H_2O$ decomposition have been used.

It is revealed that CoC_2O_4 to Co_3O_4 decomposition in air run via CoO formation (Table 2 and Fig. 1). The results of CoC_2O_4 dissociation in argon are in agreement with some the literature data e.g. [7–9] postulating formation of Co+CoO mixture as the end product.

On the basis of solid residues identification the following reactions of decomposition of CoC_2O_4 and $Co(HCOO)_2$ can be proposed:



The secondary processes can be the reduction of CoO to Co by the gas products of decomposition. The decomposition in air of $Co(HCOO)_2$ to Co_3O_4 occurs through CoO like CoC_2O_4.

Conclusions

1 – The thermal decompositions of the examined compounds are complex processes mostly in case of cobalt(II) acetate. They occur in several stages (from two to four) depending on the atmosphere and the substrate.

2 – The course of the first stage of decomposition is the same in both air and argon for each compound under investigation. This is dehydration as revealed.

3 – The next stages of the decomposition differ in air and argon.

4 – The final product of the decomposition of each compound in air is Co_3O_4. In argon it is a mixture of Co+CoO for cobalt(II) oxalate and cobalt(II) formate and CoO probably with some carbon admixture for cobalt(II) acetate.

5 – On the basis of the presented results it is considered that cobalt oxalate as well cobalt formate may be used as a precursor to obtain cobalt metal powder.

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