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COMPARISON ON THERMAL DECOMPOSITION OF PROPIONATE, BENZOATE AND THEIR CHLORODERIVATIVE SALTS OF Zn(II)

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Abstract

The thermal decompositions of propionates, benzoates Zn(II), their chloroderivate and complexes with thiourea have been studied by the means of TG, DTG, DTA, IR and XRD-powder diffraction methods. The investigated decompositions are compared and the results are presented in this report. The results showed different features of thermal decomposition of Zn(II) halogenpropionate and halogenbenzoate. In the case of Zn(II) halogenpropionate the presence of halogen effects different features of thermal decomposition and changes character of the final products. In the case of halogenbenzoate Zn(II) the halogen does not influence neither the character of decomposition nor the character of final products.

Keywords: benzoate, thermal decomposition, zinc complexes, zinc propionate

Introduction

Zinc carboxylates $[Zn(RCOO)_2]$ with or without additional ligands introduces interesting group of compounds with the potential biological activity [1, 2]. Details of preparation, identification and thermal properties of some carboxylates and halogencarboxylates Zn(II) with organic ligands have been already described in the literature [3–8]. The group of propionates, benzoates Zn(II) and their chloroderivates with thiourea is studied in this paper. The influence of presence of the halogen and thiourea and the carboxylate type on character of thermal decomposition and the character of final products is compared. The compounds of the following formulae were investigated:

$[Zn(prop)_2]$	$[Zn(benz)_2]$
$[Zn(prop)_2tu_2]$	$[Zn(benz)_2tu_2]$

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$[Zn(3\text{-}Cl\text{-}prop)_2]$ $[Zn(2\text{-}Cl\text{-}benz)_2]$

$[Zn(3\text{-}Cl\text{-}prop)_2tu_2]$ $[Zn(2\text{-}Cl\text{-}benz)_2tu_2]$

($tu=CS(NH_2)_2$, $prop=C_2H_5COO^-$, $benz=C_6H_5COO^-$)

Experimental

Synthesis of $[Zn(RCOO)_2]$ and $[Zn(RCOO)_2tu_2]$ type salts

The preparation of the studied compounds may be represented by the following reactions:

$$ZnSO_{4(aq)}+2NaOH_{(aq)} \rightarrow Zn(OH)_{2(s)}+Na_2SO_{4(aq)} \quad (1)$$

$$Zn(OH)_{2(s)}+2RCOOH_{(aq)} \rightarrow [Zn(RCOO)_2]_{(aq)}+2H_2O \quad (2)$$

$$[Zn(RCOO)_2]_{(aq)} \xrightarrow{\text{Crystallisation}} [Zn(RCOO)_2]_{(s)} \quad (3)$$

$$[Zn(RCOO)_2]_{(aq)}+2tu_{(aq)} \rightarrow [Zn(RCOO)_2tu_2]_{(aq)} \quad (4)$$

$$[Zn(RCOO)_2tu_2]_{(aq)} \xrightarrow{\text{Crystallisation}} [Zn(RCOO)_2tu_2]_{(s)} \quad (5)$$

The $Zn(OH)_2$ was prepared from $ZnSO_4\cdot 7H_2O$ (0.053 mol) with stoichiometric amount of NaOH (0.105 mol) after filtrating and washing with water Eq. (1). Prepared $Zn(OH)_2$ was dissolved in stoichiometric amounts of free carboxylic acids and evaporated up to the crystallisation in the water bath and then at the room temperature Eqs (2), (3). In the case of the $[Zn(RCOO)_2tu_2]$ synthesis, the $[Zn(RCOO)_2]$ solution prepared with the mentioned method above Eq. (2) was treated with stoichiometric amounts of thiourea and evaporated up to crystallisation at the room temperature Eqs (4), (5). The reached products of crystallisation were dried over silicagel with the yield amounts of 20–30%. Zinc was determined complexometrically.

Infrared spectroscopy

The infrared spectra of the investigated compounds were measured in the region 4000–400 cm^{-1} on a Specord M-80 spectrometer by using the KBr technique. The characteristic wavenumbers for the individual compounds are given in Table 1.

Thermal measurements

The thermal decompositions of the investigated compounds were performed on a Derivatograph OD-102 under the following experimental conditions: massed amount – 100 mg; TG – 100; DTA – 1/10; ceramic crucible; heating rate 9°C min^{-1}; static air atmosphere. The courses of thermal decomposition of the investigated compounds are presented in Figs 1, 2.

Table 1 The infrared spectral data of the studied compounds [cm^{-1}]

Assignment	Compounds							
	1	2	3	4	5	6	7	8
$\nu(N–H)_{as}$	–	3436 3416	–	3400	–	3473 3451	–	3457 3320
$\nu(N–H)_{s}$	–	3178	–	3160	–	3178 3148	–	3200
$\nu(C–H)_{ar}$	–	–	–	–	3060 3030	3077 3027	3060	3070
$\nu(C–H)$	2976 2960	3000 2984	2960	2950	–	–	–	–
$\nu(C=O)$	1630	1628	1688	1632	1630	1523	1640	1650
$\nu(C=C)_{ar}$	–	–	–	–	1595	1599	1590	1589
$\nu\begin{pmatrix}N–H\\C–S\end{pmatrix}$	–	1552 1532	–	1564 1536	–	1555 1530	–	1560 1537
$\gamma(C–H)_{ar}$	–	–	–	–	805	810	806	–
$\nu(C–Cl)$	–	–	792	770	–	–	772	795
$\nu(Zn–O)$	495	485	490	505	495	502	494	–

1 – $[Zn(prop)_2]$; 2 – $[Zn(prop)_2tu_2]$; 3 – $[Zn(3\text{-}Cl\text{-}prop)_2]$; 4 – $[Zn(3\text{-}Cl\text{-}prop)_2tu_2]$; 5 – $[Zn(benz)_2]$; 6 – $[Zn(benz)_2tu_2]$; 7 – $[Zn(2\text{-}Cl\text{-}benz)_2]$; 8 – $[Zn(2\text{-}Cl\text{-}benz)_2tu_2]$

X-ray powder diffraction

The final products of decomposition have been identified by X-ray diffractometry using CuK_α radiation. The results have been compared with JCPDS tables (Zn – JCPDS-04-0831), ZnO – JCPDS-80-0075).

Results and discussion

The preparation of the investigated compounds exhibits a number of common features with the preparation of similar carboxylates and halogencarboxylates [9]. However, some differences resulted from halogencarboxylic acids properties such as dissolution etc., have to be mentioned in this connection.

The presence of characteristic vibration of the studied compounds was proved by IR spectroscopy. IR spectra of the investigated compounds are shown in Table 1. Table 1 contains only bands of characteristic vibration which are in accordance with the literature.

The thermal decompositions have shown that only compounds $[Zn(prop)_2]$ and $[Zn(benz)_2]$ have decompositions in a one step, as it follows from Figs 1 and 2. All the other compounds are characterised by the decomposition in two steps.

On the basis results presented in Table 2 and in accordance with thermal decompositions of acetates and halogenacetates described in work [10] it is possible to suggest the following decompositions scheme.

$$[Zn(C_2H_5COO)_2] \xrightarrow{150\text{–}350°C} (C_2H_5)_2CO{+}CO_2 \xrightarrow{>350°C} ZnO_{(s)}$$

$$[Zn(CH_2ClCH_2COO)_2] \xrightarrow{110\text{–}260°C} CH_2ClCHO{+}CO \xrightarrow{300\text{–}600°C}$$

$$CH_3CHO{+}1/2H_2O{+}1/2CO{+}1/2ZnCl_2 \xrightarrow{>600°C} 1/2Zn_{(s)}$$

$$[Zn(C_2H_5COO)_2tu_2] \xrightarrow{110\text{–}300°C} 2tu{+}1/2(C_2H_5)_2CO{+}1/2CO_2 \xrightarrow{330\text{–}600°C}$$

$$1/2(C_2H_5)2CO{+}1/2CO_2 \xrightarrow{>600°C} ZnO_{(s)}$$

$$[Zn(CH_2ClCH_2COO)_2tu_2] \xrightarrow{110\text{–}320°C} 2tu{+}1/2CH_2ClCH_2CHO{+}CO \xrightarrow{320\text{–}600°C}$$

$$1/2CH_2ClCHO{+}CH_3CHO{+}CO{+}1/2ZnCl_2{+}1/2CO_2 \xrightarrow{>600°C} 1/2Zn_{(s)}$$

$$[Zn(C_6H_5COO)_2] \xrightarrow{180\text{–}250°C} (C_6H_5)_2CO{+}CO_2 \xrightarrow{>500°C} ZnO_{(s)}$$

$$[Zn(C_6H_5COO)_2tu_2] \xrightarrow{170\text{–}360°C} 2tu{+}(C_6H_5)_2CO \xrightarrow{400\text{–}700°C} CO_2 \xrightarrow{>700°C} ZnO_{(s)}$$

$$[Zn(2Cl\text{–}C_6H_4COO)_2] \xrightarrow{150\text{–}400°C} (C_6H_4Cl)_2CO \xrightarrow{400\text{–}700°C} CO_2 \xrightarrow{>700°C} ZnO_{(s)}$$

$$[Zn(2Cl\text{–}C_6H_4COO)_2tu_2] \xrightarrow{170\text{–}340°C} 2tu{+}(C_6H_4Cl)_2CO \xrightarrow{340\text{–}680°C} CO_2$$

$$\xrightarrow{>680°C} ZnO_{(s)}$$

For confirmation of the intermediate composition it is suitable to use IR spectroscopy, XRD-powder diffraction, mass spectrometry and chromatographic measurements combined with IR spectroscopy and XRD-powder diffraction. In our case the IR spectroscopy was used. The suggested thermal decompositions of prepared

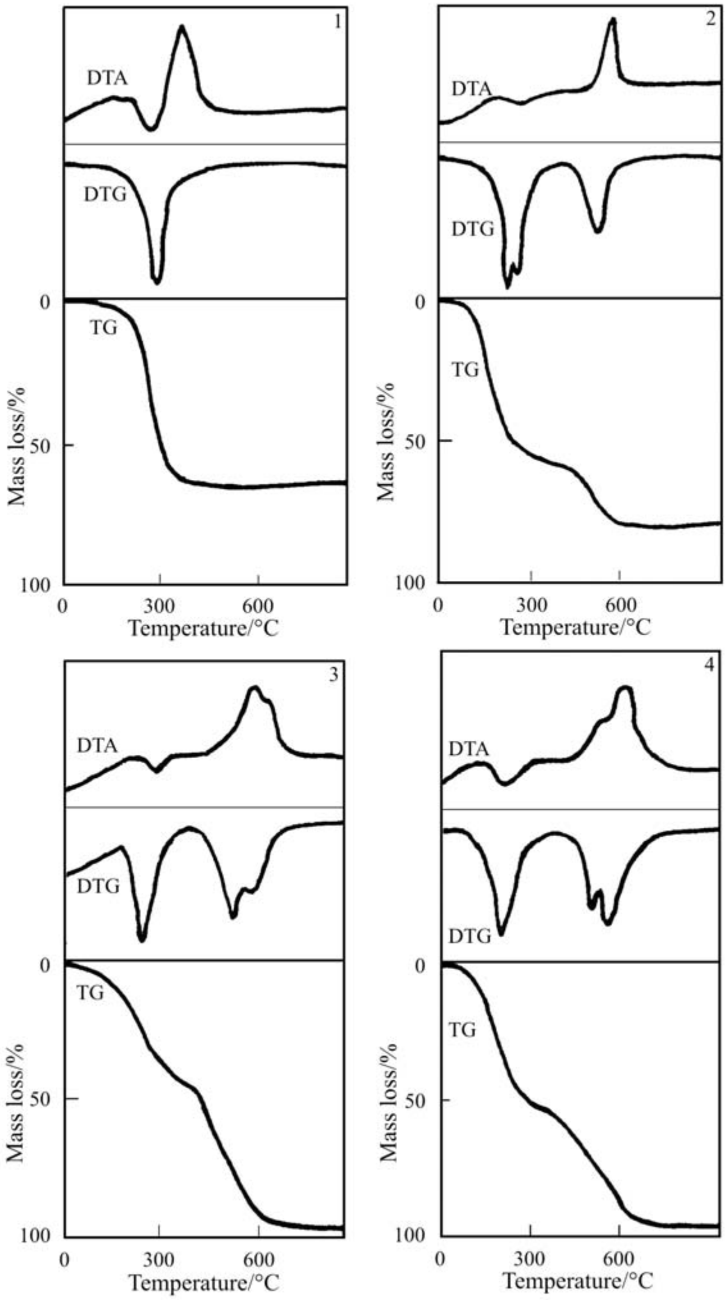

Fig. 1 Thermal decomposition of the studied compounds: 1 – $[Zn(prop)_2]$, 2 – $[Zn(prop)_2tu_2]$, 3 – $[Zn(3\text{-}Cl\text{-}prop)_2]$, 4 – $[Zn(3\text{-}Cl\text{-}prop)_2tu_2]$

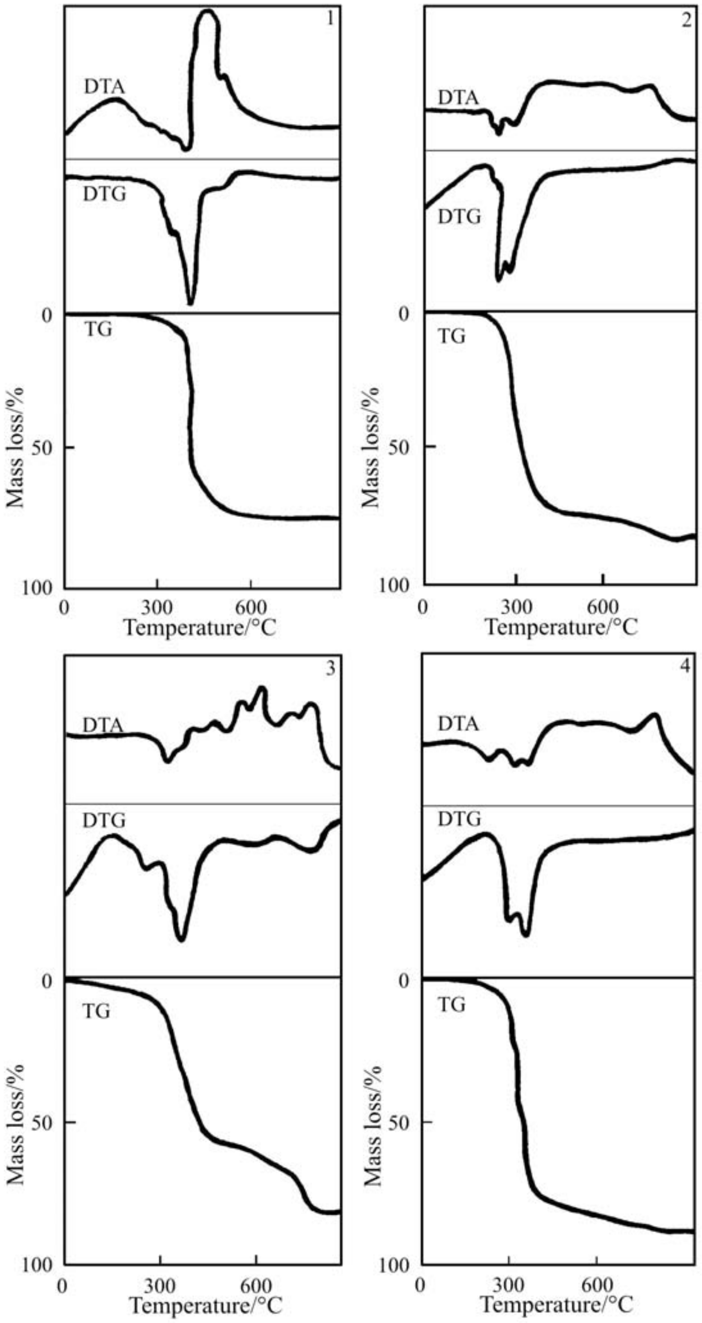

Fig. 2 Thermal decomposition of the studied compounds: 1 – [Zn(benz)$_2$], 2 – [Zn(benz)$_2$tu$_2$], 3 – [Zn(2-Cl-benz)$_2$], 4 – [Zn(2-Cl-benz)$_2$tu$_2$]

Table 2 The proposed schematics of thermal decomposition of the studied compounds

Compound	*M*	1. Mass loss			2. Mass loss			Final product		
		Liberated compound	calc/ %	obs/ %	Liberated compound	calc/ %	obs/ %		calc/ %	obs./ %
[Zn(prop)$_2$]	211.54	$(C_2H_5)_2CO+CO_2$	61.5	62	–	–	–	$ZnO_{(s)}$	38.5	38
[Zn(prop)$_2$tu$_2$]	363.7	$2tu+1/2(C_2H_5)_2CO+$ $+1/2CO_2$	59.7	61	$1/2(C_2H_5)_2CO+1/2CO_2$	17.9	18.5	$ZnO_{(s)}$	22.4	21.5
[Zn(3-Cl-prop)$_2$]	280.43	$CH_2ClCHO+CO$	38	38	$CH_3CHO+1/2HCHO+$ $+1/2CO+1/2ZnCl_2$	50.4	48	$1/2Zn_{(s)}$	11.7	12
[Zn(3-Cl-prop)$_2$tu$_2$]	432.67	$2tu+$ $1/2ClCH_2COCH_3$	47.6	47	$1/2CH_2ClCHO+CO+1/2CO_2$ $+CH_3CHO+1/2ZnCl_2$	46.6	46	$1/2Zn_{(s)}$	7.6	9
[Zn(benz)$_2$]	307.62	$(C_6H_5)_2CO+CO_2$	73.5	73	–	–	–	$ZnO_{(s)}$	26.5	27
[Zn(benz)$_2$tu$_2$]	459.87	$2tu+(C_6H_5)_2CO$	72.7	71	CO_2	9.6	10	$ZnO_{(s)}$	17.7	18
[Zn(2-Cl-benz)$_2$]	376.51	$(C_6H_4Cl)_2CO$	66.7	67	CO_2	11.7	12	$ZnO_{(s)}$	21.6	21
[Zn(2-Cl-benz)$_2$tu$_2$]	528.76	$2tu+(C_6H_4Cl)_2CO$	76.3	77	CO_2	8.3	8	$ZnO_{(s)}$	15.4	15

compounds are in accordance with IR spectral data of the presumed intermediates. IR spectral data of the intermediates are not presented in this paper. The results presented in Table 2 and Figs 1 and 2 refer to different features of the thermal decompositions of propionates, benzoates and their chloroderivates.

In the case of propionates without a presence of Cl the final product of decomposition is ZnO. The Cl presence causes the formation of $ZnCl_2$ during thermal decomposition. Consequently, the created $ZnCl_2$ is evaporated ($ZnCl_2$ *m.p.* 262°C, *b.p.* 732°C) thus Zn remains as the final product.

In the case that Cl is not present, the organic components are released in a form of ketones. Otherwise (in Cl presence) they are released as aldehydes. Similar decompositions of Zn(II) acetates have been observed [10–12].

Benzoates and chlorobenzoates of Zn(II) are decomposed in the same way, the organic compounds are released in the form of ketones, irrespective of the Cl presence ZnO has been identified using the XRD-powder diffraction as the final product.

The common feature of the decompositions is the fact that thiourea is always released during the first step of decompositions [13].

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