

Use of emanation thermal analysis and evolved gas analysis in thermal study of zinc(II) benzoate complex compounds

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Abstract Thermal behaviours of three zinc(II) benzoate complex compounds (two new with caffeine and urea), namely $\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2$, $\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2\cdot\text{caf}_2$, $\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2\cdot\text{u}_2$, were characterized by using thermogravimetry (TG/DTG), differential thermal analysis (DTA), evolved gas analysis (EGA) with mass spectrometry (MS) detection and emanation thermal analysis (ETA). Temperature intervals of the stability of the compounds as well as the mechanisms of their thermal degradation were determined. From TG and DTA results it followed that the oxidative degradation of urea with CO_2 or caffeine with CO_2 from the investigated Zn(II) benzoate complex compounds takes place as the first step of their thermal degradation. In the second step of thermal degradation diphenylketone was release. The evolved gas analysis has been used to determine intermediate products of thermal degradation and temperature ranges of their evolution from the samples. From the emanation thermal analysis results it followed that changes in the surface area and microstructure accompanied the thermal degradation of the

compounds studied and that no microstructure changes can be supposed in the resulting zinc oxide on heating from 650 up to 850 °C.

Keywords Zinc(II) benzoate · Caffeine · Urea · Thermogravimetry · Differential thermal analysis · Emanation thermal analysis · Evolved gas analysis

Introduction

Zinc(II) carboxylate complex compounds with N- or O-donor organic ligands are of practical interest because of their potential biological activity. Zinc has structural, chemical and regulatory role in biological systems, it is an essential ingredient of the active site in many enzymes [1]. Zn^{2+} ions strongly interacts with electronegative sulphur, nitrogen, oxygen, nevertheless it does not promote the formation of toxic radicals [2]. The interaction of benzoic and salicylic acids with metal ions has been commonly studied in relation to environmental, antimicrobial and medical problems [3]. In the recent years we have studied the biological, thermal and spectral properties of some zinc(II) aromatic and aliphatic carboxylates with N- and O-donor ligands [4–8]. The thermal degradation of zinc(II) benzoate $\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2$ was studied by Gusejnov et al. [9].

In this paper the thermal behaviours of zinc(II) benzoate and zinc(II) benzoate complex compounds with caffeine and urea, namely $\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2$, $\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2\cdot\text{caf}_2$, $\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2\cdot\text{u}_2$ are described. Thermal analysis methods, like thermogravimetry, differential thermal analysis, evolved gas analysis with mass spectrometry detection and emanation thermal analysis were used for this purpose.

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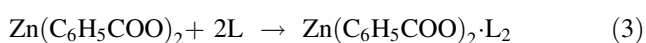
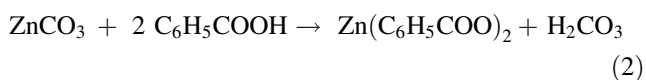
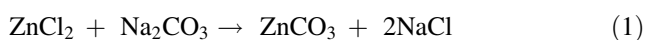
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Experimental

Samples and their preparation

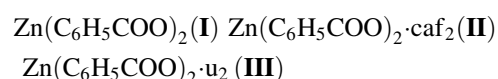
Zinc(II) benzoate and two newly prepared zinc(II) benzoate complex compounds with caffeine and urea, respectively were studied. Following A. R. grade chemicals were used for the samples preparation: ZnCl₂ p.a., Na₂CO₃ p.a. (Lachema Neratovice), benzoic acid 99% (Aldrich), urea and caffeine (Merck). The synthesis of the compounds is expressed by following equations:



where

$L = \text{caf}$ or u .

ZnCO₃ was prepared by using solutions of the stoichiometric amounts of ZnCl₂ and Na₂CO₃ as described in Eq. 1. The water–alcohol solution of carboxylic acid was added to the water suspension of ZnCO₃ under continual stirring in hot water at 70 °C. After one hour, the solution of zinc(II) benzoate was filtered off and the aqueous solution of a ligand (caffeine, urea) was added to the filtrate. The reaction mixture was stirred for 3 h, then filtered off and left to stand to crystallize at room temperature. After several days white crystals were formed as a precipitate. The precipitates of the formed Zn(II) benzoate complex compounds were filtered off, washed with water and dried over silicagel. The compounds of the following formula were prepared:



Where abbreviations *caf* is for caffeine and *u* is for urea.

The yields of the reaction were 82% for the compound denoted as (I), 92% for the compound denoted as (II) and 78% for the compound denoted as (III) [10]. Elemental analysis, FTIR spectroscopy and mass spectrometry were used to characterize the samples composition.

Methods used for samples characterization

Infrared spectra were measured by the Perkin Elmer Spectrophotometer (in the range 4,000–400 cm⁻¹ using KBr pellets) and by the Bruker Vertex 70 FTIR Spectrophotometer (in the range 1,100–200 cm⁻¹ using CsI technique).

TG, DTA and EGA with MS detection were carried out by using the simultaneous NETZSCH STA 424 equipment

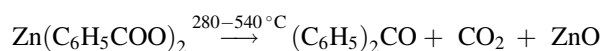
coupled with QMS BALZERS. The sample (amount of 0.02 g) was placed in an alumina crucible and heated at the rate of 5 °C/min in an air flow (flow rate 60 mL/min).

ETA [11–13], based on the measurement of the release of radon atoms from solids, was performed by using the NETZSCH DTA–ETA Equipment, Model 404. Radon ²²⁰Rn atoms were introduced into the samples due to the recoil energy (85 keV atom⁻¹) gained during α-spontaneous decay of ²²⁸Th and ²²⁴Ra. The samples were previously labeled by adsorption of ²²⁸Th and ²²⁴Ra as nitrates from an acetone solution and the acetone solvent was dried out after five minutes. The specific activity of the sample was 10⁵ Bq per gram. The maximal penetration depths of the recoiled ²²⁰Rn atoms in the zinc(II) benzoate complexes studied was 100 nm as calculated by Monte Carlo method by using TRIM code [14]. The samples (amount 0.05 g) were heated in the temperature range 20–950 °C at the rate of 6 °C/min in a constant air flow (flow rate 50 mL/min). The measured values of the radon release rate, *E*, are presented (in relative units) as $E = A_\alpha/A_{\text{total}}$, where *A*_α is α-radioactivity of radon released in unit time from the labeled sample, and *A*_{total} is the total γ-radioactivity of the labeled sample. The *A*_{total} value is proportional to the rate of radon formation in the sample. Semiconductor and NaI (TI) detectors were used for α- and γ-radioactivity measurements, respectively. ETA was used to characterize microstructure changes and the thermal behaviour of the samples in their subsurface up to 100 nm labelled with radon atoms.

Results and discussion

Thermal behaviour of Zn(C₆H₅COO)₂

TG/DTG, DTA and EGA results of the zinc(II) benzoate compound Zn(C₆H₅COO)₂ are presented in Fig. 1. From the TG results it is obvious that the sample is stable up to 280 °C. The release of (C₆H₅)₂CO and CO₂ was characterized by the mass decrease in the temperature range 280–540 °C as demonstrated on the TG curve in Fig. 1. From the DTA curve in Fig. 1 it followed that exothermic effects were observed at 423 and 476 °C, respectively. The release of (C₆H₅)₂CO was confirmed by IR spectra and by mass spectrometry results. It was found that after heating the sample to 330 °C, the absorption band of carboxylate group ν_{as}(COO⁻) at 1,638 cm⁻¹ was missing. The release of CO₂ (*m/z* = 44) was confirmed in temperature range 361–532 °C by mass spectra (for MS data see Fig. 1). The residue mass values of the final degradation product ZnO as well as of the intermediate products of the thermal degradation are presented in Table 1. The following mechanism is proposed for the thermal decomposition of compound Zn(C₆H₅COO)₂:



Unlike the zinc(II) benzoate for barium benzoate the final product is BaCO_3 [15].

The ETA results made it possible to determine the radon permeability in the subsurface of the sample, that was labeled by radon atoms to the depths of 100 nm. In the temperature range from 30 to 285 °C where no mass loss was observed (Fig. 1), the diffusion of radon was characterized by an increase on ETA curve. In the temperature range 285–300 °C the decrease of the radon diffusion was observed reflecting probably melting of the sample. This is in agreement with the DTA endothermic effect observed at 325 °C. The increase of the radon release rate in the range from 350–400 °C can be ascribed to loosening of the structure of the sample caused by its thermal degradation. The break on the ETA curve observed at 400 °C corresponds to the point when the thermal degradation of the sample subsurface was over; the thermal degradation of the sample bulk continued up to 540 °C as it was indicated by

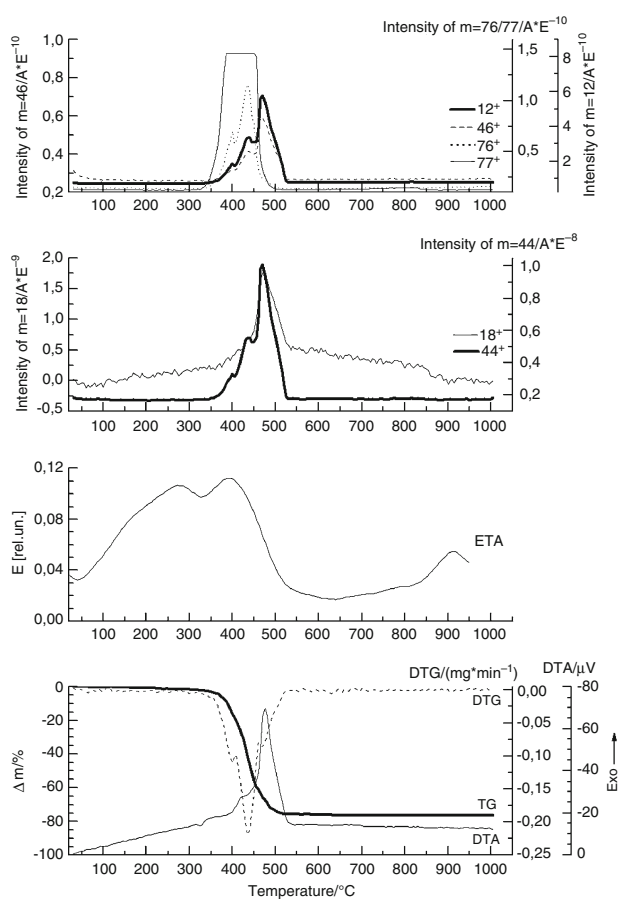
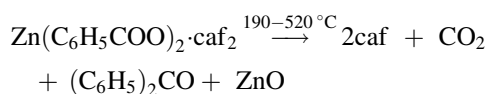


Fig. 1 Results of thermogravimetry (TG/DTG), differential thermal analysis (DTA), evolved gas analysis (EGA) with MS detection and emanation thermal analysis (ETA) of the compound $\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2$ measured on heating in air

the release of volatile products and a mass loss. The radon release rate decreased continuously in this temperature range, as it is obvious from the ETA curve. The zinc oxide as a solid product of the thermal decomposition was characterized by a relatively low value of the radon release rate. The increase of the radon release $E(T)$ on heating above 650 °C was due to the radon diffusion by volume mechanism in the zinc oxide sample. From the exponential character of the ETA curve (Fig. 1) it can be expected that no microstructure changes occurs in the resulting zinc oxide up to 850 °C. From the break observed on the ETA curve in Fig. 1 we assumed that on further heating the growth of grains or sintering of the finely powdered zinc oxide sample occurs on heating above 900 °C.

Thermal behaviour of $\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2 \cdot \text{caf}_2$

From TG results presented in Fig. 2 it followed that the thermal decomposition of $\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2 \cdot \text{caf}_2$ starts at 190 °C. Two mole of caffeine and one mole of CO_2 were released in the temperature range 190–360 °C as indicated by TG results and by an endothermic effect at 220 °C on DTA curve. The experimentally found mass loss in this temperature range are summarized in Table 1. The release of caffeine was confirmed by IR spectra measured up to 290 °C, where the characteristic bands of caffeine $\nu(\text{C}=\text{O})$ at $1,704\text{ cm}^{-1}$, $\nu(\text{C}=\text{N})$ at $1,657\text{ cm}^{-1}$ and $\nu(\text{C}-\text{H})_{(\text{CH}_3)\text{caff}}$ at $2,949\text{ cm}^{-1}$ were missing. The next mass loss step in the range 360–520 °C corresponds to the release of $(\text{C}_6\text{H}_5)_2\text{CO}$ (for the mass loss values see Table 1). This step is accompanied by a strong DTA exothermic effect with maximum 462 °C. The intermediate products $(\text{C}_6\text{H}_5)_2\text{CO}$ and CO_2 were confirmed by mass spectra. The CO_2 starts to release at 256 °C ($m/z = 44$) and C_6H_5^+ starts to release at 306 °C ($m/z = 77$) (for MS data of the volatile products see Fig. 2). ZnO resulted as the solid final product of the thermal decomposition and residue mass values are summarised in Table 1. The following reaction is proposed for the thermal decomposition of the compound $\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2 \cdot \text{caf}_2$:



The radon permeability in the subsurface of the sample can be determined from the ETA results. In the temperature range from 30 to 185 °C, where no mass loss was observed, the diffusion of radon was characterized by an increase on ETA curve due to its thermal desorption (Fig. 2). In the temperature range 190–280 °C the decrease of the radon release rate reflected the liberation of caffeine from the sample. The increase of the radon release rate observed from 290 to 380 °C can be ascribed to the loosening of the structure of the sample caused by its thermal

Table 1 Intermediates and final products of the thermal decomposition of the zinc(II) benzoate complexes

Compound	Temperature range of decomposition/°C	Products of thermal decomposition	Mass loss/%		Residue mass	
			exp.	calc.	exp.	calc.
Zn(C ₆ H ₅ COO) ₂	280–540	(C ₆ H ₅) ₂ CO + CO ₂	73.10	73.54	26.90	26.46
Zn(C ₆ H ₅ COO) ₂ ·caf ₂	190–360	2caf + CO ₂	60.57	62.13	10.85	11.69
	360–520	(C ₆ H ₅) ₂ CO	28.58	26.18		
Zn(C ₆ H ₅ COO) ₂ ·u ₂	128–340	2u + CO ₂	37.00	38.37	18.70	19.03
	340–605	(C ₆ H ₅) ₂ CO	44.30	42.60		

caf caffeine, u urea

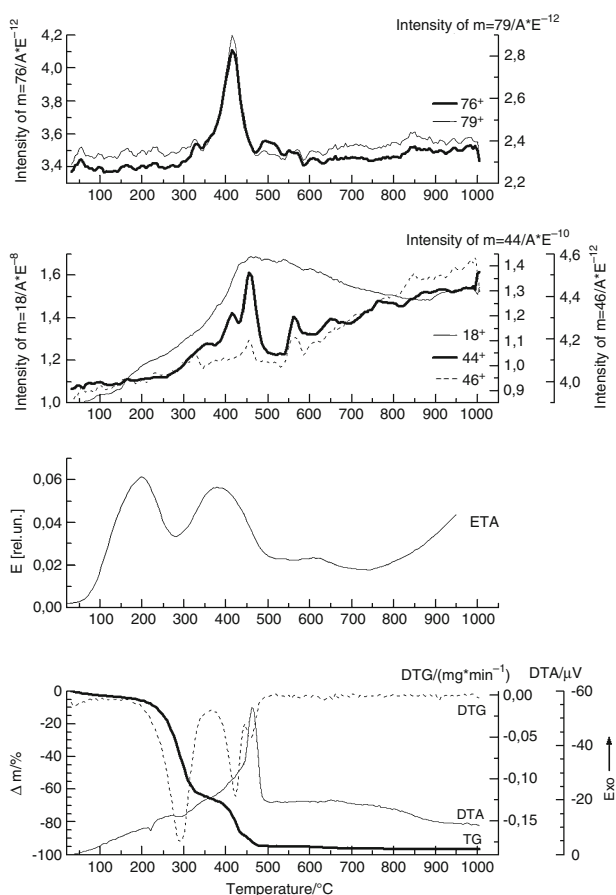
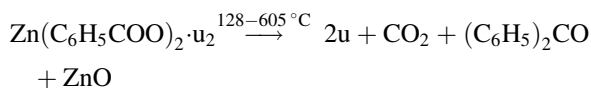


Fig. 2 Results of thermogravimetry (TG/DTG), differential thermal analysis (DTA), evolved gas analysis (EGA) with MS detection and emanation thermal analysis (ETA) of the Zn(C₆H₅COO)₂·caf₂ compound measured on heating in air

degradation. The break on the ETA curve at 400 °C corresponds to the next step of the thermal degradation of the sample. It is in agreement with the results of mass spectrometry and the DTA exothermic effect, corresponding to the thermal degradation processes. From the exponential-like character of the temperature dependence of the radon release rate $E(T)$ in Fig. 2 it followed that no microstructure changes occurs on heating from 650 to 1,050 °C in zinc oxide formed after the thermal degradation of the Zn(II) benzoate complex compound with caffeine.

Thermal behaviour of Zn(C₆H₅COO)₂·u₂

From Fig. 3 it followed that the thermal decomposition of Zn(C₆H₅COO)₂·u₂ takes place in two steps. The compound is thermally stable up to 128 °C. In the first step in the temperature range 128–340 °C two mole of urea and one mole of CO₂ were released, the corresponding experimental and calculated mass loss values are presented in Table 1. The release of urea in the first step was confirmed by IR spectra of solid intermediates measured up to 160 °C, where the characteristic absorption bands $\nu_{as}(\text{N-H})_u$ at 3,404 cm⁻¹, $\nu_s(\text{N-H})_u$ at 3,316 cm⁻¹ and $\nu(\text{C=O})$ at 1,647 cm⁻¹ were missing [10]. In the second step the (C₆H₅)₂CO was released in the temperature range 340–605 °C. The (C₆H₅)₂CO decomposed to the ions C₆H₅CO⁺ ($m/z = 105$) and C₆H₅⁺ ($m/z = 77$) [10]. This step is accompanied with two exothermic effects on the DTA curve at 455 and 497 °C. The final product of thermal decomposition is ZnO. The following mechanism is proposed for the thermal decomposition of the Zn(C₆H₅COO)₂·u₂ compound:



From the ETA results in Fig. 3 it followed that the pre-melting of the sample, characterized by the break and the subsequent decrease of the radon release rate, took place on heating from the temperature of 120 °C. The increase of radon release in the range from 130 °C up to 350 °C reflected a loosening of the structure due to release of the volatile products from the sample during its thermal degradation. The break at 400 °C and the following decrease of the radon release rate accompanied the next step of the thermal degradation of the sample as reflected by the volatile products detected by MS and by the DTA exothermic effect. Zinc oxide as the solid residue after thermal degradation of Zn(C₆H₅COO)₂·u₂ is characterized by a relatively low value of radon release rate $E(T)$. The exponential like character of the $E(T)$ dependence on heating above 750 °C is due to the radon diffusion by volume mechanism; we assume that no considerable

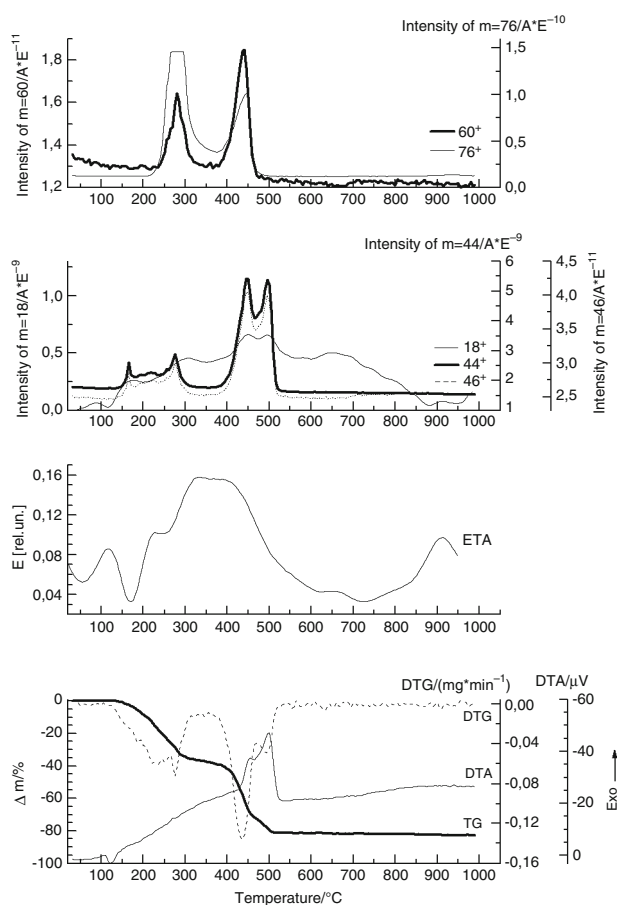


Fig. 3 Results of thermogravimetry (TG/DTG), differential thermal analysis (DTA), evolved gas analysis (EGA) with MS detection and emanation thermal analysis (ETA) of the $\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2 \cdot \text{u}_2$ compound measured on heating in air

morphology changes took place in the zinc oxide up to 850 °C. The break and subsequent decrease of radon release rate $E(T)$ on heating above 900 °C makes it possible to expect the growth or sintering of fine grains of the zinc oxide powder prepared by the thermal degradation of the Zn(II) benzoate complex with urea.

Conclusions

It was found that the oxidative degradation of urea with CO_2 or caffeine with CO_2 from the investigated Zn(II) benzoate complex compounds takes place as the first step of their thermal degradation. In the second step of thermal degradation diphenylketone was release.

Intermediate products of thermal degradation of the zinc(II) benzoate complex compound were determined by evolved gas analysis. Microstructure changes that accompanied the degradation of the samples were characterized by emanation thermal analysis on heating. Zinc oxide was determined as the final product of thermal degradation after

heating the compounds to 600 °C. From the smooth exponential-like increase of the radon release rate observed by ETA on sample heating from 650 up to 850 °C it followed that no microstructure changes can be expected with the zinc oxide samples in this temperature range. The break and subsequent decrease of radon release rate observed by ETA on heating above 900 °C makes it possible to assume the growth or sintering of fine grains of the zinc oxide powders.

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