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THERMAL DECOMPOSITION OF CADMIUM SUCCINATE DIHYDRATE

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Thermal decomposition of cadmium succinate dihydrate, $CdC_4H_4O_4{\cdot}2H_2O$, was studied in dynamic helium and air atmospheres by means of simultaneous TG, DTA and MS analysis. It was found that dehydration of $CdC_4H_4O_4{\cdot}2H_2O$ takes place in the temperature range 80–165°C and at low heating rates formation of monohydrate was stated.

The anhydrous cadmium succinate decomposes at about 350°C to metallic cadmium. The gaseous products of cadmium succinate decomposition are CO_2 and H_2O. Formation of small amounts of 3-phenylpropanal and 1,7-octadiene during decomposition in helium was revealed. In helium cadmium evaporates at the temperature of decomposition and the residue consists of small amount of elementary carbon formed in result of pyrolysis of succinate groups. In air cadmium oxidizes and the final solid product of decomposition is CdO.

Keywords: *cadmium succinate dihydrate, DTA, MS analysis, TG, thermal decomposition*

Introduction

Thermal properties of cadmium salts are not often investigated due to the high toxicity of Cd. However cadmium salts are useful in industry, pharmacology and analysis. Cadmium carboxylates and bicarboxylates are used as catalysts, colorants, stabilizers [1, 2] and in ^{113}Cd NMR spectroscopy of biological systems [3]. Recently cadmium carboxylates, together with dimethyl sulfoxide, are used as precursors of nanocrystalline CdS for photocells and luminous paints [4]. Authors of the present paper took up studies on thermal decomposition of the series of cadmium carboxylates and bicarboxylates to reveal the influence of cation and anions on this process. The results on mechanism of decomposition of cadmium acetate and malonate hydrates were published earlier [5, 6]. In the present work we report on preparation, structural identification and thermal characterization of cadmium succinate dihydrate.

The cadmium succinate has two stable hydrates described in the literature – diaquacadmium succinate, $Cd(H_2O)_2C_4H_4O_4$, [7] and diaquacadmium succinate hemihydrate, $Cd(H_2O)_2C_4H_4O_4{\cdot}0.5H_2O$ [8]. Both have monoclinic, polymer structure with seven-coordinated Cd atoms. The structure of $Cd(H_2O)_2C_4H_4O_4$ is best described as a distorted pentagonal dipyramid with the cadmium atom and five oxygen atoms (these O atoms belong to three succinate ligands) in the equator and two oxygen atoms of the water molecules out of plane. Three succinate ligands are connected to Cd atom through bidentate (the two of the ligands) or monodentate (the third one) interaction. The Cd atoms are bridged by oxygen atoms which take part in the bidentate and in the monodentate interactions. This structure is stabilised into two-dimensional polymer by hydrogen bonds between the water molecules and the oxygen atoms belonging to the succinate groups. The structure of $Cd(H_2O)_2C_4H_4O_4{\cdot}0.5H_2O$ is also described by pentagonal dipyramid, but in this structure two crystallographically independent seven-coordinate Cd atoms exist, chelated by succinate ligands. One of the chelating oxygen atoms belonging to carboxyl groups makes a bridge between two cadmium atoms, while the other end of the same succinate ligand is used to form three-dimensional polymer structure.

Thermal decomposition of cadmium succinate dihydrate was investigated in oxygen [7] and air [9]. It was found that at temperature about 150°C, because of dehydration, $CdC_4H_4O_4{\cdot}2H_2O$ transforms to anhydrous and amorphous cadmium succinate. At 262°C this amorphous product turned into crystalline $CdC_4H_4O_4$. Decomposition of $CdC_4H_4O_4$ proceeded with formation of intermediate as $CdCO_3$ [7] or $CdO{\cdot}CdCO_3$ [9]. The final product of decomposition is CdO.

The aim of this paper is to describe the thermal behaviour of cadmium succinate dihydrate in inert (helium) atmosphere, determine the intermediate product of decomposition in air as well as determine gaseous products of decomposition.

Experimental

Material

Cadmium succinate dihydrate was prepared by mixing a hot, aqueous solution of succinic acid, $C_4H_6O_4$, and an 15% aqueous solution of cadmium acetate,

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$Cd(CH_3COO)_2$, in molar ratio 1:1. All reagents used were pure for analysis and delivered by P.O.Ch. Gliwice S.A. The received solution was filtered off and left for a period of one month for the crystallisation process. The formed crystals were washed with distilled water to remove the residue of acetic acid and cadmium acetate, filtered off and dried at 60°C in dryer. After grinding in an agate mortar, the fraction of 10–100 μm grain size was separated for further investigation. The sample was kept in a desiccator over CaO during the whole process of investigations.

Methods

Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out on SDT 2960 (TA Instruments) apparatus. The samples of mass around 10 mg were placed in standard platinum crucibles and heated with rates 2, 5 and 10°C min^{-1}. The course of decomposition was independent on the heating rate therefore results for the heating rate 5°C min^{-1} were chosen for presentation. The measurements were carried out under dynamic conditions (the flow of 100 cm^3 min^{-1}) in helium (purity 99.999%) and synthetic air atmospheres (<15 ppm H_2O).

The gaseous products of reactions were analyzed with the quadrupole mass spectrometer QMD 300 Thermostar (Balzers) operated with an electron impact ionizer with energy 0.112 aJ (70 eV). The measurements were performed in scan mode for m/z (where m is mass of molecule and z is a charge of the molecule in electron charge units) range from 10 to 118, which is the mass of succinic acid molecule. The mass spectrometer was connected on-line with SDT apparatus by the heated (up to 200°C) quartz capillary.

The composition of the initial sample, intermediates and residue was analyzed by Phillips X-ray diffractometer using CuK_α radiation. IR spectra were recorded on BIO-RAD FTS60V spectrometer using the KBr pellet technique. EDS analysis was performed using JMS-5400 (JEOL) scanning electron microscope.

Results and discussion

The compound obtained was investigated using XRD and IR analysis. The X-ray pattern for the initial sample (Fig. 1) was the same as pattern of $CdC_4H_4O_4{\cdot}2H_2O$ published in [10] and IR spectrum (Fig. 2) was identical as this published in [7].

Figures 3 and 4 present TG, DTA and MS results obtained in helium and in air, respectively.

Dehydration

The first DTA signal corresponds to the dehydration process. The mass change is 13.7% in relation to theoretical change 13.62%. In air dehydration is a single step process however the DTA peak is broad and irregular. In helium the double DTA peak of dehydration appeared which results from the separation of water molecules evolution. In experiments performed at heating rates 2 and 5°C min^{-1} in the first step 1.5 water molecules are lost, and at heating rate

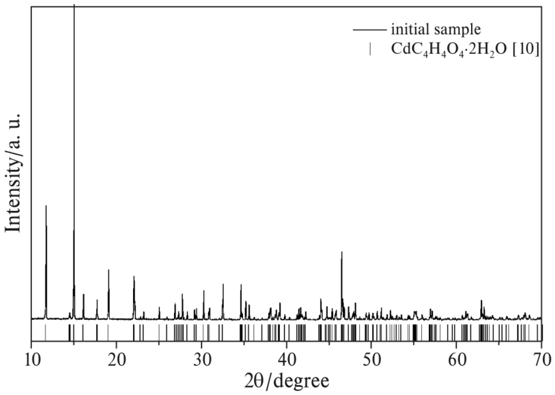

Fig. 1 XRD pattern of initial sample

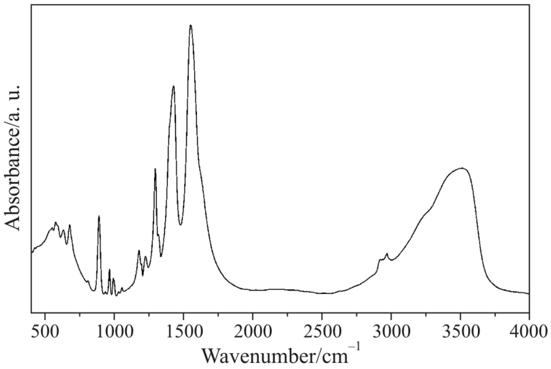

Fig. 2 IR spectrum of initial sample

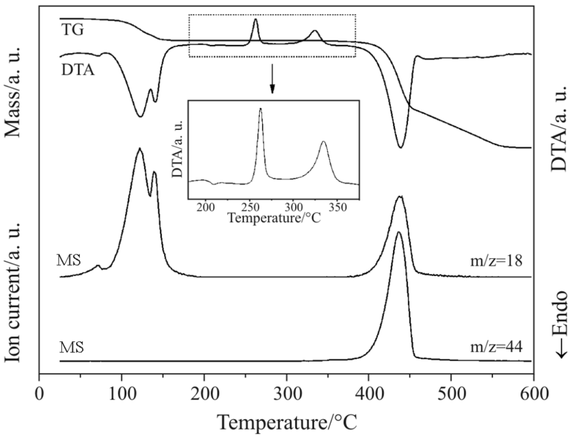

Fig. 3 TG, DTA results of $CdC_4H_4O_4{\cdot}2H_2O$ decomposition in helium (5°C min^{-1}) and MS signals of CO_2 and H_2O

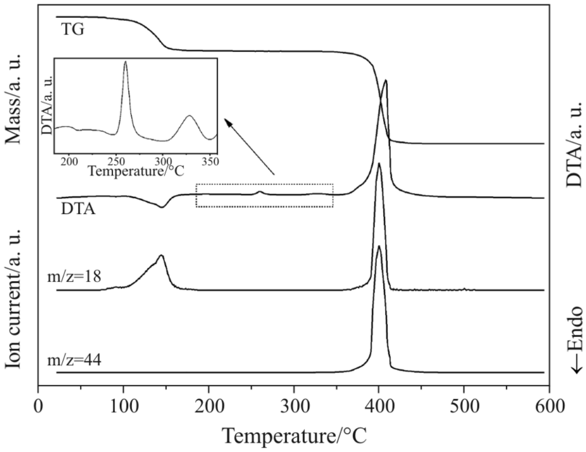

Fig. 4 TG, DTA results of $CdC_4H_4O_4{\cdot}2H_2O$ decomposition in air (5°C min^{-1}) and MS signals of CO_2 and H_2O

10°C min^{-1} in the first step one water molecule is evolved (Fig. 5). This can be the result of the existence of two hydrogen bonds between one water molecule and oxygen atoms of succinate moiety while the second water molecule is involved in one hydrogen bond with a succinate group and is weakly hydrogen bonded to the second water molecule [7].

Phase transitions

After dehydration which finishes at about 165°C no changes of mass are observed till 350°C. In this temperature range however phase transitions of anhydrous cadmium succinate occur. First is connected with glass transition of amorphous phase obtained after dehydration. For this phase the XRD pattern does not reveal any signals (Fig. 6). This transition is observed in the temperature range 200–215°C and is manifested by the characteristic step on the DTA curve. Next at 262 and at 332°C the exothermic DTA peaks occur corresponding to crystallization of the sample. Figure 6 shows the XRD patterns recorded for sample at 270°C after first exothermic DTA peak, at 285°C and at 345°C after second exothermic DTA peak. Sample at 270°C is well crystallized however is not structurally stable and on further heating undergoes some kind of structural transformation accompanied by exothermic effect. In result at 345°C the sample has different XRD pattern than at 270°C.

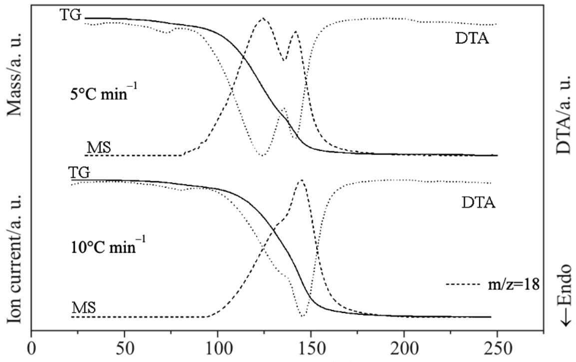

Fig. 5 Dehydration of $CdC_4H_4O_4{\cdot}2H_2O$ in helium

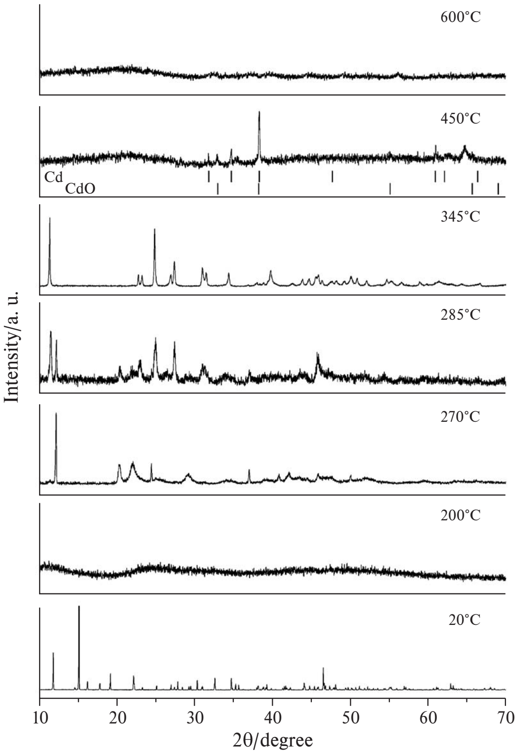

Fig. 6 XRD pattern of initial $CdC_4H_4O_4{\cdot}2H_2O$ and samples from different temperatures (helium)

Decomposition in helium

Decomposition of anhydrous $CdC_4H_4O_4$ in helium starts at about 350°C. The mass loss observed is 71.2%. This can be compared with theoretical mass loss 43.8% when assuming CdO as the final product or 50.8% when assuming Cd as the final product of decomposition. Actually the product of decomposition of cadmium succinate is cadmium but it instantaneously melts as the temperature of decomposition is higher than the melting temperature of Cd (321°C). Melted cadmium evaporates as the temperature rises.

On the TG curve of $CdC_4H_4O_4$ decomposition two stages of mass loss are seen. The first stage is accompanied by endothermic DTA peak and evolution of gaseous products of decomposition. No effects on DTA curve as well as no gases were observed for the second stage of mass loss. Therefore it can be stated that the first stage on TG curve corresponds mainly to decomposition while the second one corresponds to evaporation of cadmium. Cadmium vapour condensed on the cool parts of thermobalance and could not be detected by the mass spectrometer.

In the residue after decomposition in helium at 600°C cadmium is not present but only elementary carbon was detected (Fig. 7). Elementary carbon is produced in result of pyrolysis of succinate groups. XRD pattern of the sample at 600°C reveals no signals and is characteristic for amorphous material.

The main gaseous products of $CdC_4H_4O_4$ decomposition are CO_2 (m/z=44) and H_2O (m/z=18). Assuming intensity of CO_2 signal as 100%, the intensity of H_2O signal was 27%. In the spectrum of gaseous products of decomposition a lot of signals were detected but their intensity was below 0.8%. After comparing relative intensities of all MS signals, 3-phenylpropanal, $C_9H_{10}O$, and 1,7-octadiene, C_8H_{14}, were identified in the gas phase over decomposing sample. Table 1 contains mass spectra of 3-phenylpropanal and 1,7-octadiene taken from NIST database [11] and Figs 8 and 9 show intensities of experimental m/z signals which were assigned to these gases. As the content of carbon per molecule in $C_9H_{10}O$ and C_8H_{14} is higher than in succinate group it means that this compounds formed during pyrolysis of succinate groups in reaction of condensation. Signals m/z=55, 56, 73 and 74 have intensities higher than these resulting from fragmentation of 3-phenylpropanal or 1,7-octadiene. These signals originate most probably from fragmentation ions of succinate groups.

Taking above considerations into account the course of cadmium succinate decomposition in inert atmosphere is as follows:

$$CdC_4H_4O_4 \rightarrow Cd+(CO_2, H_2O, C_9H_{10}O, C_8H_{14}, C)$$

Decomposition in air

Decomposition of $CdC_4H_4O_4$ in air starts at about 350°C and is accompanied by strong exothermic effect. The reaction is completed at 450°C. The experimental mass loss is 43.6% and is almost the same as theoretical mass loss calculated for decomposition to

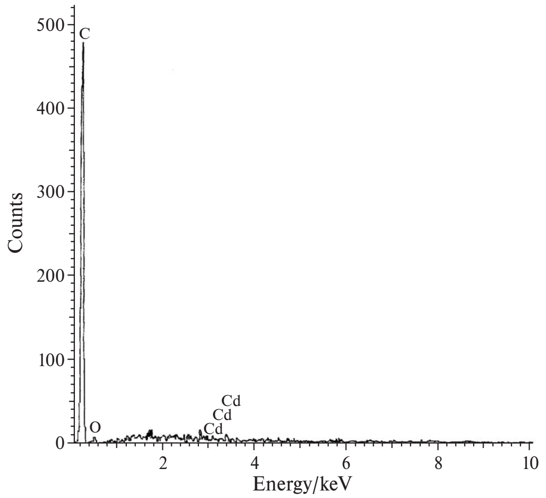

Fig. 7 EDS analysis of the residue of $CdC_4H_4O_4 \cdot 2H_2O$ decomposition in helium

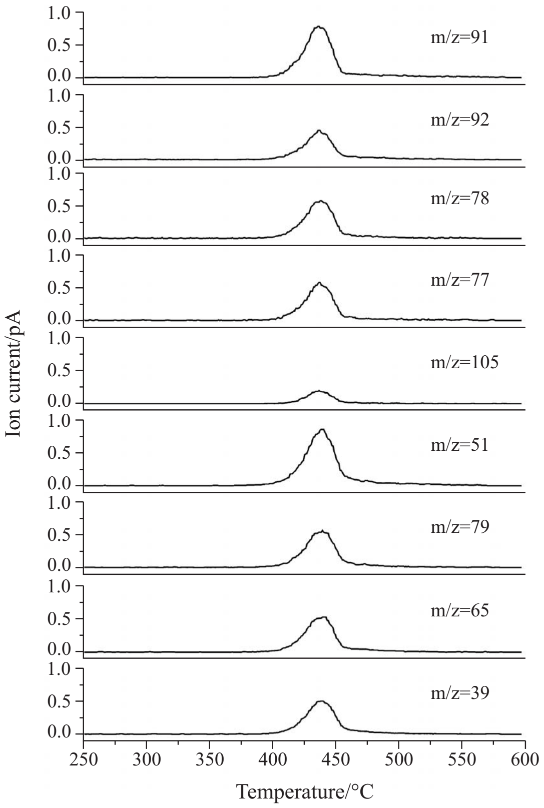

Fig. 8 The intensities of experimental m/z signals corresponding to 3-phenylpropanal

Table 1 Mass spectra* [11]

Compound	Mass spectrum m/z (intensity)
$C_9H_{10}O$	91(100) 92(82.1) 78(51.8) 134(49.6) 77(35.7) 105(31.0) 51(28.3) 79(25.1) 65(22.0) 39(20) 103(15.4) 50(13.5) 27(11.5) 63(11.1) 133(9.5) 29(7.7) 52(6.6) 115(6.4) 104(5.7) 55(5.6) 93(5.5) 116(5.3) 89(4.8) 135(4.7) 74(4.6) 76(4.2) 38(3.8) 62(3.7) 106(3.6) 102(3.2) 56(3.1) 53(3.0) 75(2.8) 28(2.6) 64(2.5) 41(2.4) 15(1.9) 26(1.8) 37(1.7) 66(1.7) 80(1.6) 117(1.5) 40(1.4) 107(1.4) 61(1.2) 43(1.0)
C_8H_{14}	41(100) 54(60.0) 67(52.5) 39(47.6) 27(31.9) 82(26.8) 68(22.7) 81(19.2) 55(18.9) 29(15.9) 53(13.6) 95(10.3) 69(9.7) 40(7.5) 28(7.4) 42(6.6) 56(4.1) 26(4.0) 15(3.8) 51(3.8) 66(3.6) 79(3.5) 38(3.4) 43(2.7) 65(2.4) 50(2.0) 52(1.8) 83(1.8) 77(1.7) 94(1.3) 37(1.2) 80(1.0) 96(1.0)

*only signals with intensities >1 were given

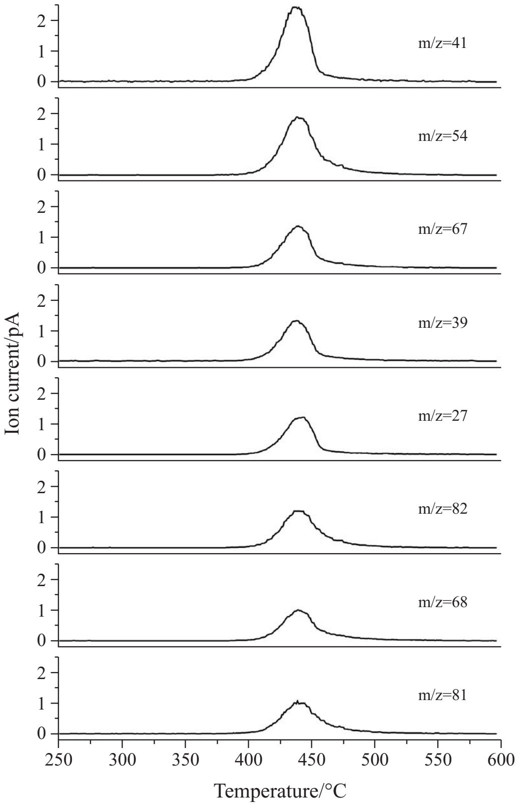

Fig. 9 The intensities of experimental *m*/*z* signals corresponding to 1,7-octadiene

CdO. CdO was confirmed as the final product by XRD analysis. No intermediate phases were found. The gaseous products were only CO_2 and H_2O.

The maximum of DTA peak appears at 408°C, which is temperature 8°C higher than the maxima of CO_2 and H_2O signals. This is the result of two consecutive reactions occurring: first is decomposition of $CdC_4H_4O_4$ to Cd, and next – oxidation of Cd to CdO. The first reaction is endothermic one however the presence of oxygen makes it oxidative decomposition. The second one is strongly exothermic. In result of superposition of three thermal effects the irregular DTA peak with maximum at temperature of maximum speed of Cd oxidation was observed.

The course of $CdC_4H_4O_4$ decomposition in air is as follows:

$$CdC_4H_4O_4+3.5O_2 \rightarrow CdO+4CO_2+2H_2O$$

Conclusions

Thermal decomposition of cadmium succinate dihydrate is two-stage reaction, dehydration and decomposition of anhydrous compound. These stages are clearly separated. Anhydrous cadmium succinate is amorphous and undergoes glass transition and two crystallization processes. Decomposition of anhydrous crystalline cadmium succinate leads to cadmium as the final solid product and carbon dioxide and water as the main gaseous products of decomposition. In inert atmosphere cadmium evaporates at the temperature of decomposition whereas in oxygen containing atmosphere it oxidizes to CdO. The residue after decomposition in inert atmosphere is elementary carbon resulting from pyrolysis of succinate groups. The products of pyrolysis are also 3-phenylpropanal, $C_9H_{10}O$, and 1,7-octadiene, C_8H_{14}, which small amounts were found in the gas phase over cadmium succinate decomposing in inert atmosphere. Formation of organic compounds with high molecular mass during decomposition of *d*-metal carboxylates has been already reported in [6, 12, 13].

Acknowledgements

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