

THERMAL DECOMPOSITION OF $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ STUDIED BY A COUPLED TG-DTA-MS METHOD

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Abstract

The thermal decomposition of cadmium acetate dihydrate in helium and in air atmosphere has been investigated by means of a coupled TG-DTA-MS method combined with X-ray diffraction analysis. Dehydration of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ is a two-stage process with $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ as intermediate. The way of $\text{Cd}(\text{CH}_3\text{COO})_2$ decomposition strongly depends on the surrounding gas atmosphere and the rate of heating. CdO, acetone and CO_2 are the primary products of decomposition in air. In helium decomposition goes by two parallel and consecutive reactions in which intermediates, Cd and CdCO_3 , are formed. Metallic cadmium oxidizes and cadmium carbonate decomposes giving CdO. Some of the metallic cadmium, depending on the heating rate and the concentration of oxygen, evaporates. Acetone is partially oxidized in secondary reactions with oxygen.

Keywords: cadmium acetate, dehydration, evolved gas analysis, thermal decomposition

Introduction

d-electron metal salts containing organic anions such as oxalates, acetates, formates etc. are common precursor systems for the controlled synthesis of *d*-metal oxides or alloys under mild conditions. The mechanism of thermal decomposition of anhydrous or hydrated metal salts is important in determining the properties of the solid product.

A few studies have been published for different cations with the acetate anion [1–5]. The hydrates of *d*-electron metal acetates decompose in two main consecutive steps: dehydration and decomposition of the anhydrous salt. After dehydration, however, basic salts are sometimes formed [6]. The decomposition of acetates strongly depends on the surrounding atmosphere. Depending on the conditions the solid product can be the metal or/and the metal oxide. On decomposition acetates often yield acetone and acetic acid. In addition some other volatile products have been reported like CO_2 , CO, methane, isobutene and acetaldehyde [7].

The decomposition of cadmium acetate has not been investigated previously except for a kinetic study [8]. At 130°C the compound becomes anhydrous. The anhydrous cadmium acetate melts at about 250°C and between 250–280°C decomposes [9].

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Cadmium acetate dihydrate is a complex compound. The cadmium interacts with seven oxygens (Cd–O distances range from 229.4 to 259.7 pm), two from the waters of hydration and five from the acetate groups [10]. The co-ordination polyhedron of oxygen atoms around the central metal atom is best described as a distorted square base-trigonal capped polyhedron (idealized C_5 symmetry). Both of the acetate groups are bidentate, but an oxygen atom in one of them is also in a bridging position forming a continuous cadmium-oxygen spiral around the two-fold screw axis parallel to *c*. Both acetate groups are planar. The oxygen atoms of each acetate ion can be regarded as three-co-ordinate. The compound is extensively hydrogen-bonded. All oxygen atoms and water hydrogen atoms are involved.

In the presented work the thermal decomposition of cadmium acetate dihydrate under non-isothermal conditions was studied to reveal the mechanism of the process.

Experimental

Commercial $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ of analytical grade (Polskie Odczynniki Chemiczne S.A.) was used. The experiments were carried out on TA Instruments SDT 2900 simultaneous thermal analyzer connected with Balzers QMD 300 Thermostar quadrupole mass spectrometer for detection of gaseous products of reaction. The samples were heated in a standard platinum crucible. The measurements were carried out under dynamic conditions in inert and oxidizing atmospheres (helium or synthetic air). The flow of $100 \text{ cm}^3 \text{ min}^{-1}$ was controlled using a mass-flow controller. The heating rates used were 2 and 5°C min^{-1} . Some experiments were performed at $20^\circ\text{C min}^{-1}$. Mass of the samples ranged between 8 and 11 mg.

The composition of the solid intermediates and the final products of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ decomposition were analyzed by means of an X-ray diffractometer using CuK_α radiation (Seifert XRD-7).

Results and discussion

All the results from TG, DTA and MS analysis are normalized. TG-DTA signals obtained during the decomposition of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in helium and in air at the heating rate 5°C min^{-1} are presented in Fig. 1.

Dehydration of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$

The TG curves for experiments carried out in air are quite different from those for experiments performed in helium. The TG curve obtained during heating $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in air exhibits three steps. The first two steps can be attributed to the dehydration of the dihydrate. The only MS signals detected for this process were of $m/z=18$, 17 and 16 corresponding to the mass spectrum of water. In each of the steps the mass loss corresponds to the evolution of one molecule of H_2O for each molecule of cadmium acetate. The steps on the TG curve are accompanied by separate endotherms on the DTA curve. In helium atmosphere the dehydration proceeds in the same

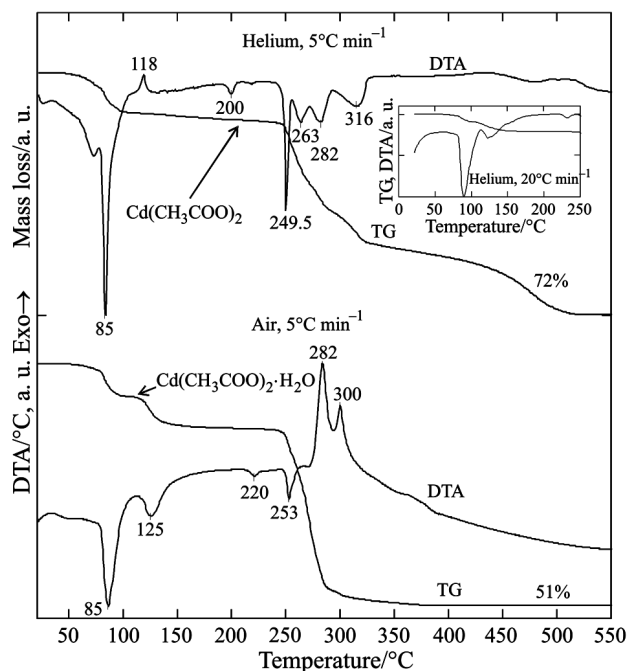


Fig. 1 TG and DTA curves for the decomposition of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in helium and air atmospheres at a heating rate of 5°C min^{-1} . The inset presents the results of dehydration at the heating rate of $20^\circ\text{C min}^{-1}$

way as in air however the separation of two dehydration steps on the TG curve is noticed at higher heating rates. The stepwise loss of two water molecules is in accordance with the crystal structure of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, where the two water molecules are bound in non-equivalent positions around the metal [10]. Dehydration is complete at about 180°C . XRD analysis confirmed the presence of anhydrous $\text{Cd}(\text{CH}_3\text{COO})_2$ in samples cooled down from 180 and 200°C .

The exotherm at about 120°C observed in all experiments with inseparable dehydration steps can be attributed to the recrystallization of amorphous cadmium acetate which occurs after dehydration connected with melting of the sample. No significant change in the TG curve at this temperature is noticed as well as no mass spectrometric signal.

The continuous mass loss in the TG curve between 100 and 240°C (more noticeable for the measurements in helium) indicates the evolution of some volatile substance.

Before the beginning of the decomposition of $\text{Cd}(\text{CH}_3\text{COO})_2$ the DTA curves show endotherms at 200 and 220°C , for measurements in helium, and at 220°C for measurements in air, which are not connected with changes in the TG curve. These endotherms could result from some phase transitions of anhydrous cadmium acetate, however very thorough X-ray diffraction analysis of the sample performed in a high temperature camera did not confirm the presence of any different phases. DSC scans

for anhydrous cadmium acetate in the range 120–230°C made during heating and then during cooling showed that these effects are irreversible.

Decomposition of $\text{Cd}(\text{CH}_3\text{COO})_2$ in air

The decomposition of anhydrous cadmium acetate is preceded by melting of the sample accompanied by an endotherm with a maximum at about 250°C (according to NIST data, the melting temperature of anhydrous $\text{Cd}(\text{CH}_3\text{COO})_2$ in air is 256°C). For the decomposition carried out in air the total loss of mass of 51% is in good agreement with the 51.8% mass loss calculated for CdO as the final solid product. XRD analysis confirmed this result. At about 380°C decomposition is complete. On the DTA curve, except for the endotherm corresponding to the melting of sample, two exotherms are present. The endothermic effect of the decomposition seems to be superimposed on the exothermic effect of some process and this results in DTA curve having a horizontal segment in the temperature range of decomposition.

The mass spectrum of the gas over the decomposing cadmium acetate contained the following m/z signals: 12, 14, 15, 16, 17, 18, 25, 26, 27, 28, 29, 30, 31, 32, 37, 38, 39, 40, 41, 42, 43, 44, 45, 53, 55, 56, 57, 58, 59, 60, 83 and 95. The main gases identified are: acetone $\text{CH}_3\text{—CO—CH}_3$ (mass spectrum: 14, 15, 25, 26, 27, 28, 29, 31, 37, 38, 39, 40, 41, 42, 43 – 100%, 53, 55, 57, 58, 59), CO_2 (mass spectrum: 12, 16, 28, 44 – 100%), H_2O (mass spectrum: 16, 17, 18 – 100%) and vapors of acetic acid (mass spectrum: 15, 29, 42, 43 – 100%, 45, 60).

Figure 2 shows the signals $m/z=18$, 43 and 44 characteristic of water, acetone and carbon dioxide, respectively. The composition of the gaseous phase over the decomposing cadmium acetate depends strongly on the carrier gas. However, both in helium and in air acetone is formed mainly in the beginning of the decomposition.

In order to connect the volatile products with the stage of the decomposition the degree of evolution of different gases was determined from the intensities of the ion currents using the procedure described elsewhere [11] and the degree of conversion was determined from the TG curve. Figures 3 and 4 show the calculated degrees of evolution of CH_3COCH_3 , CO_2 , H_2O and CH_3COOH and the degree of conversion.

For decomposition in air atmosphere the degree of conversion corresponds with the degree of evolution of acetone, which indicates that the main mass loss is related to the formation and evolution of acetone. Thus during decomposition in air the following reaction occurs:



The degree of evolution of CO_2 should be the same as the degree of evolution of acetone, however, it is lower during the whole course of decomposition. Additionally the maximum intensity of CO_2 occurs 20°C above the temperature of the first maximum of the acetone intensity (Fig. 2). These effects as well as the presence of water and acetic acid in the gaseous phase (Fig. 5 shows signal of $m/z=60$ which is characteristic for acetic acid) indicate that the following secondary reactions can take place:



and



These are catalytic reactions occurring probably on the surface of cadmium oxide or on the surface of the platinum crucible and can explain the exotherms in the DTA curve. Thus CO₂ results not only from the primary reaction of Cd(CH₃COO)₂

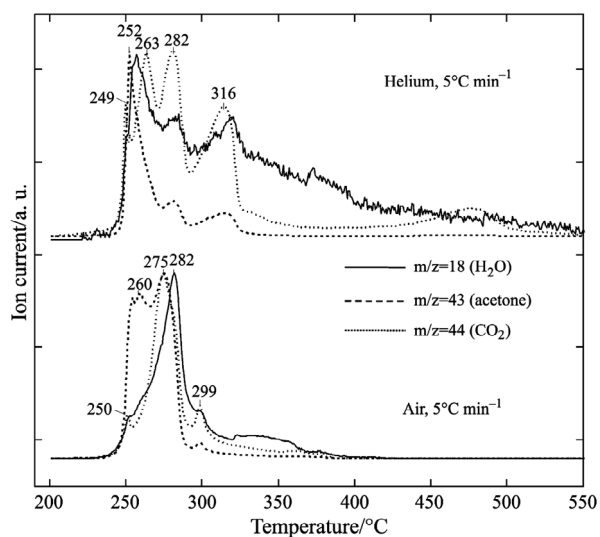


Fig. 2 Selected MS signals for the decomposition of Cd(CH₃COO)₂ in helium and air atmospheres at a heating rate of 5°C min⁻¹

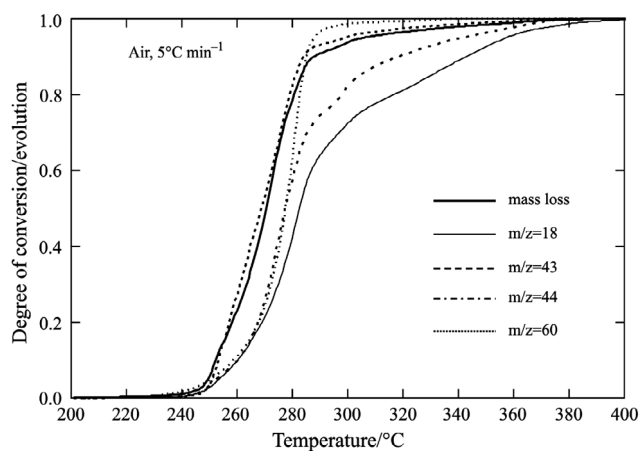


Fig. 3 The degree of evolution of volatile products and the degree of conversion for the decomposition of Cd(CH₃COO)₂ in air

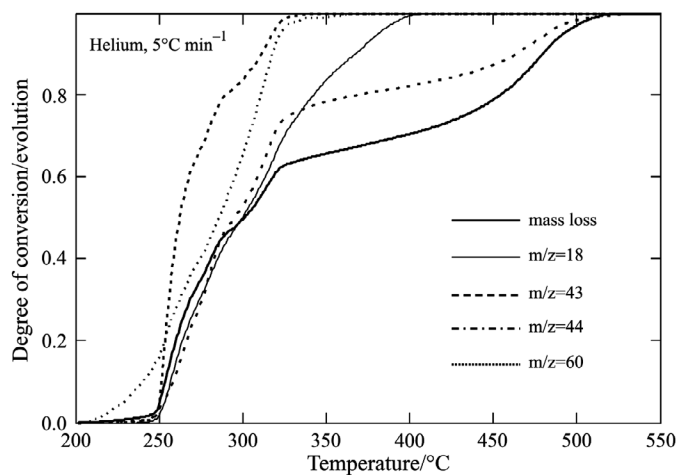


Fig. 4 The degree of evolution of volatile products and the degree of conversion for the decomposition of $\text{Cd}(\text{CH}_3\text{COO})_2$ in helium

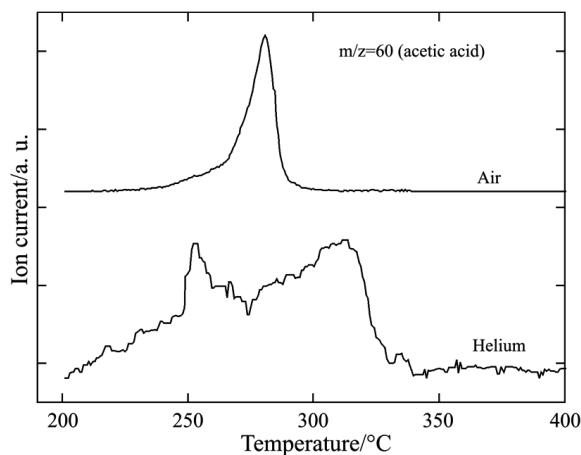


Fig. 5 The MS signal for $m/z=60$ characteristic for acetic acid detected during decomposition of $\text{Cd}(\text{CH}_3\text{COO})_2$ in helium and air atmospheres at a heating rate of 5°C

decomposition, but also from the secondary reactions of the oxidation of acetone which are delayed in relation to the primary reaction. The total amount of CO_2 is greater than that resulting from $\text{Cd}(\text{CH}_3\text{COO})_2$ decomposition. This explains the differences between the degrees of evolution of CO_2 and of acetone.

Decomposition of $\text{Cd}(\text{CH}_3\text{COO})_2$ in helium

Decomposition of $\text{Cd}(\text{CH}_3\text{COO})_2$ in helium is quite different. Decomposition begins at about 250°C . The TG curve shows several overlapping steps with corresponding

endotherms on the DTA curve. All the mass changes are completed by about 520°C, almost 200°C higher than in the experiments carried out in air. The total mass change of 72% is much higher than the mass loss of 57.8% calculated for the formation of metallic Cd (Fig. 1). This suggests that some part of the cadmium vaporizes. XRD analysis showed that the solid residue from decomposition at 550°C is CdO.

The MS analysis showed the presence of the same signals as for decomposition in air. The main amount of acetone is evolved until 280°C and the main amount of CO₂ is produced when acetone disappears (Fig. 2). The evolution of acetone and acetic acid ends at about 350°C, while CO₂ and H₂O are detectable in the gas phase up to 520°C.

When the decomposition of Cd(CH₃COO)₂ proceeds in helium, the degree of conversion is much lower than the degree of evolution of acetone during the whole course of reaction (Fig. 4). The large mass loss is thus not only a consequence of acetone evolution, but also results from the evolution of some volatile substance far later than evolution of acetone occurs.

The solid residue sampled at several temperatures in the region 280–350°C is composed mainly of CdO and of traces of metallic cadmium (Fig. 6) which was observed only in few diffractograms. The formation of metallic cadmium during decomposition of cadmium acetate in helium was confirmed in another experiment, where 5 g sample of Cd(CH₃COO)₂ was placed in quartz tube and was heated in the flow of helium. On the cold ends of the tube some black powder condensed which was found to be metallic Cd.

Metallic Cd thus forms one of the solid products of Cd(CH₃COO)₂ decomposition in helium according to the following equation:



The oxygen which forms during this reaction was observed in experiments performed at high heating rates (Fig. 7).

The metallic cadmium formed during decomposition is very active and reacts instantaneously with the oxygen formed in the same reaction, or with traces of oxygen present in the inert atmosphere:



The temperature of melting of cadmium is 321°C [12]. The cadmium vapor pressure close to this temperature is relatively high and rises as the temperature increases. The extra mass loss observed thus results from the vaporization of the part of metallic cadmium formed during decomposition. The rate of vaporization depends on the rate of heating.

The MS signal *m/z*=44 corresponding to CO₂ reveals four peaks. All these peaks can be ascribed to four endothermic effects on the DTA curve having extrema at the same temperatures. The peaks with maxima at 249, 282 and 316°C correspond with the peaks on the MS signal for acetone (Fig. 1). However, the degree of evolution of CO₂ is significantly lower than the degree of evolution of acetone during the whole course of decomposition. In addition evolution of CO₂ is complete by 520°C while

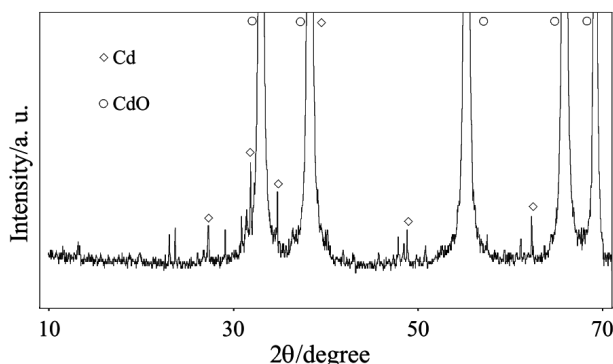


Fig. 6 The XRD pattern of the solid residue taken at 350°C during the decomposition $\text{Cd}(\text{CH}_3\text{COO})_2$ in helium

acetone is not detectable above 350°C. All these observations indicate that there must be another compound which decomposes giving CO_2 .

The most probable explanation is the formation of CdCO_3 in a parallel reaction:



The cadmium carbonate formed is assumed to be amorphous because XRD analysis performed *in situ* in a high-temperature camera did not reveal any other phases than CdO and Cd . The grains of CdCO_3 can decompose on the surface up to 350°C:



The remaining CdCO_3 decomposes between 450–500°C that is confirmed by a small peak on the CO_2 signal, the endothermic effect on the DTA curve and the mass

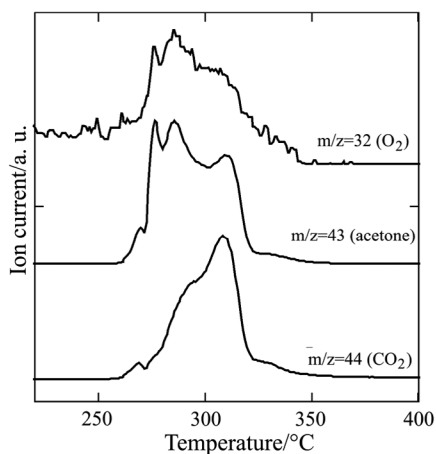


Fig. 7 The MS signals for oxygen, acetone and carbon dioxide observed during the decomposition of $\text{Cd}(\text{CH}_3\text{COO})_2$ in helium at a heating rate of $20^\circ\text{C min}^{-1}$

loss on the TG curve. The total amount of CdO at the end of reaction at 520°C results from the oxidation of metallic Cd and decomposition of CdCO_3 .

The presence of small amounts of water and acetic acid in the gas over the reacting cadmium acetate results from oxidation of acetone as proposed for the decomposition in air – Eqs (2) and (3). This explains the decrease in the intensity of $m/z=32$ signal in the temperature range of decomposition in the experiments carried out with low heating rates.

Some comments should be made on the evolution of acetic acid. From Fig. 4 we see that evolution of acetic acid begins before the start of decomposition. These small amounts of acetic acid could arise at a result of hydrolysis of cadmium acetate in the presence of the crystallization water. When the temperature rises the acetic acid evaporates but some of it can be trapped in the occlusions and be liberated at higher temperatures.

No reliable explanation for the weak mass spectrometric signals of $m/z=56$, 83 and 95 can be given. The presence of ions of that high mass is evidence that some secondary processes between gaseous products occur, but in a very small scale.

Conclusions

This study of the thermal decomposition of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in helium and in air atmospheres has revealed the complexity of this process. The dehydration of the dihydrate proceeds by two stages with the formation of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ as an intermediate.

The path of decomposition of $\text{Cd}(\text{CH}_3\text{COO})_2$ depends strongly on the surrounding atmosphere, as well as on the heating rate. The decomposition of $\text{Cd}(\text{CH}_3\text{COO})_2$ in air leads to the formation of CdO as a solid product and acetone and carbon dioxide as the gaseous products. The decomposition of $\text{Cd}(\text{CH}_3\text{COO})_2$ in helium occurs by two parallel reactions. In the first reaction the solid product is metallic cadmium and the gaseous products are acetone, carbon dioxide and oxygen. In the second reaction cadmium carbonate and acetone are formed. CdCO_3 then decomposes and metallic Cd oxidizes. The final product of cadmium acetate decomposition in helium atmosphere is CdO. Some of the metallic cadmium evaporates and its amount depends on the heating rate and on the rate of oxidation of cadmium.

In air, and to a lesser extent in helium, secondary reactions between the gaseous products occur, mainly oxidation of acetone.

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