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THERMOGRAVIMETRICAL STUDY ON SOME CRYSTAL HYDRATES OF METAL(II) BENZOATES

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ABSTRACT

The following salts are studied thermogrvimetrically: $Ca(C_6H_5COO)_2.3H_2O$, $Mg(C_6H_5COO)_2.4H_2O$, $Mn(C_6H_5COO)_2.2H_2O$, $Co(C_6H_5COO)_2.4H_2O$, $Ni(C_6H_5COO)_2.4H_2O$, $Cu(C_6H_5COO)_2.3H_2O$. It is found that up to 200°C the crystal hydrates lose their crystallization water and form corresponding anhydrous salts. The TG and DTG curves show that with the exception of $Mn(C_6H_5COO)_2.2H_2O$, the dehydration of the metal benzoates takes place gradually. The anhydrous salts are characterized by IR-spectra. The thermal decomposition of the anhydrous salts begins at temperature higher than 220°C and the corresponding metal oxides or metals are formed.

In this study, we have examined the mode of thermal dehydration and decomposition of some metal(II) benzoates $Me(C_6H_5COO)_2.nH_2O$ by TG, DTA and DTG (Me = Ca, Mg, Mn, Co, Ni, Cu). The experiments were carried out using a Paulik-Paulik-Erdey apparatus in an atmosphere of air. The heating rate was 10°C min^{-1}. About 200-300 mg samples were placed in the sample holder with an equal weight of reference material (Al_2O_3). The results have also been supported by X-ray diffraction and IR-emission spectrometry.

The salts were prepared by treating metal(II) carbonates with benzoic acid at high temperature and by mixing molar solutions of metal(II) salts (chlorides, sulfates) and molar sodium benzoate solutions at room temperature (at ratio 1:2). The salts were stirred in their saturated solutions at 25°C in a thermostat for several days.

The experimental results of this study are shown in Table 1.

It is found that up to 200°C the crystal hydrates lose their crystallization water and form the corresponding anhydrous salts. The loss of water above 200°C can be used as an indicator that the water molecules are coordinated to the metal ions.

The TG and DTG curves show that with the exception of $Mn(C_6H_5COO)_2.2H_2O$, the dehydration of the metal benzoates takes place gradually.
$Ni(C_6H_5COO)_2.4H_2O$ and $Co(C_6H_5COO)_2.4H_2O$ lose three water molecules in the first step of dehydration and the last water molecule in the second one. For $Mg(C_6H_5COO)_2.4H_2O$ two water molecules are lost per step. $Ca(C_6H_5COO)_2.3H_2O$ and $Cu(C_6H_5COO)_2.3H_2O$ lose two and a half water molecules in the first step.

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TABLE 1

Metal benzoates	Initial dehydration temperature	Temperature range of anhydrous salt stability	End temperature of decomposition	End products
$Ca(C_6H_5COO)_2.3H_2O$	70	170 - 420	740	CaO
$Mg(C_6H_5COO)_2.4H_2O$	90	-	670	MgO
$Mn(C_6H_5COO)_2.2H_2O$	100	155 - 325	600	MnO
$Co(C_6H_5COO)_2.4H_2O$	75	200 - 270	610	$Co_3O_4+Co_2O_3$
$Ni(C_6H_5COO)_2.4H_2O$	100	-	510	Ni
$Cu(C_6H_5COO)_2.3H_2O$	80	200 - 220	950	Cu

The anhydrous salts are characterised by IR-spectra. In the region 3100-3700 cm^{-1} the IR-spectra do not display a band near 3600 cm^{-1} and this fact confirm the claim that simple anhydrous salts are formed (not hydroxy benzoates).

It is known that nickel benzoate crystallizes with three water molecules /1/. The present thermogravimetrical study shows that the nickel benzoate crystallizes with four water molecules and it is isostructural with the $Co(C_6H_5COO)_2.4H_2O$ (their X-ray diffraction patterns and IR-spectra are identical).

Some anhydrous salts are stable in a comperatively large temperature interval - $Ca(C_6H_5COO)_2$, $Mn(C_6H_5COO)_2$, $Co(C_6H_5COO)_2$, $Cu(C_6H_5COO)_2$, but for some anhydrous salts no temperature interval of stability is observed - $Ni(C_6H_5COO)_2$, $Mg(C_6H_5COO)_2$.

The thermal decomposition of the anhydrous salts begins at temperatures higher than 220^oC (about 220^oC for copper benzoate and about 420^oC for calcium benzoate). The thermal decomposition is accompanied with a melting of the anhydrous salts. The end products of the thermal decomposition are oxides - CaO, MgO, MnO, Co_3O_4 (mixed with Co_2O_3) or metals - Ni, Cu. The thermal decomposition of $Cu(C_6H_5COO)_2.3H_2O$ have been studied up to 350^oC and the end product proved to be CuO /2/. In the case of calcium benzoate $CaCO_3$ is formed as an intermediate product.

The dehydration and decomposition of the metal(II) benzoates can be expressed as follows:

$$Ca(C_6H_5COO)_2.3H_2O \xrightarrow{-2\frac{1}{2}H_2O} Ca(C_6H_5COO)_2.\tfrac{1}{2}H_2O \xrightarrow{-\frac{1}{2}H_2O} Ca(C_6H_5COO)_2 \rightarrow CaCO_3 \rightarrow CaO$$

$$Mg(C_6H_5COO)_2.4H_2O \xrightarrow{-2H_2O} Mg(C_6H_5COO)_2.2H_2O \xrightarrow{-2H_2O} Mg(C_6H_5COO)_2 \longrightarrow MgO$$

$$Mn(C_6H_5COO)_2.2H_2O \xrightarrow{-2H_2O} Mn(C_6H_5COO)_2 \longrightarrow MnO$$

$$Co(C_6H_5COO)_2 \cdot 4H_2O \xrightarrow{-3H_2O} Co(C_6H_5COO)_2 \cdot H_2O \xrightarrow{-H_2O} Co(C_6H_5COO)_2 \rightarrow Co_3O_4 + Co_2O_3$$

$$Ni(C_6H_5COO)_2 \cdot 4H_2O \xrightarrow{-3H_2O} Ni(C_6H_5COO)_2 \cdot H_2O \xrightarrow{-H_2O} Ni(C_6H_5COO)_2 \rightarrow NiO \rightarrow Ni$$

$$Cu(C_6H_5COO)_2 \cdot 3H_2O \xrightarrow{-2\frac{1}{2}H_2O} Cu(C_6H_5COO)_2 \cdot \tfrac{1}{2}H_2O \xrightarrow{-\frac{1}{2}H_2O} Cu(C_6H_5COO)_2 \rightarrow CuO \rightarrow Cu_2O \rightarrow Cu$$

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