Thermochimica Acta, 93 (1985) 53-56
Elsevier Science Publishers B.V., Amsterdam

THERMAL BEHAVIOUR OF METAL p-HYDROXYBENZOATES

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ABSTRACT

The thermal decomposition of divalent metals as Mg,Mn,Co,Ni, Zn,Cd p-hydroxybenzoates had been investigated in dynamic conditions under air in temperature range 20-1000°C.The solid state intermediate and resultant products of thermolysis had been identified.The possible scheme of destruction of the complexes is suggested.The X-ray single crystal structure analysis has shown that Mg,Mn,Co,Ni,Zn p-hydroxybenzoates do form the series of isostructural compounds of the composition $[M(H_2O)_6]L_2 2H_2O$. By means of X-ray powder analysis the structure of the intermediate thermolysis products had been studied.

INTRODUCTION

The reveal of the relationship between the structure and thermolysis of metal carboxylate complexes,the study of the influence of metal and ligand nature on the process of thermal decomposition are of a certain interest.But the reported data on thermal decomposition of the complexes with aromatic carboxylate ligands are too rare.There had been studied the thermal decomposition of some Cu complexes/1-3/ and alkali metals/4,5/ with benzoic acid derivatives.In the present work there are given the results of X-ray and thermogravimetric studies of metal p-hydroxybenzoates.

MEASURING METHODS

Preparation of the complexes. The complexes had been synthesised by mixing in 1:2 ratio at room temperature of the aquaous solutions of chlorides and sulphates of the corresponding metals and Na p-hydroxybenzoate at pH of the solution 6-7.The composition of the complexes had been determined by element analysis: $ML_2 \cdot 8H_2O$ (M=Mg,Mn,Co,Ni,Zn; $L=p-HOC_6H_4COO^-$), $CdL_2 \cdot 7H_2O$.

Proceedings of ICTA 85, Bratislava

Thermogravimetry. The process of thermal destruction of the complexes had been investigated on Hungarian MOM-model at heating rate 10°C/min. Al_2O_3 was used as ethalone. The measurement had been carried out in covered Pt crucible. To identify the solid state intermediates and resultant products of thermolysis the isothermic calcination of the complexes had been carried out at different temperatures.

X-ray analysis. The X-ray powder analyses had been done on Dron-2-model(λCu-K_α -radiation, V=32 kv, I=20 mA). The crystal structures had been solved by heavy atom method and refined anisotropically by least square procedure. For the compounds studied there has been collected as the three-dimensional data intensity set by using fourcircle automatic difractometer "Syntex $P2_1$" (θ-2θ scantechnique, λMo-K_α -radiation).

RESULTS AND DISCUSSION

The X-ray analyses had shown/6/ that Mg,Mn,Co,Ni,Zn p-hydroxybenzoate octahydrates form the series of isostructural compounds, their structures being of symmetrical octahedron aquaions $[M(H_2O)_6]^{2+}$(except cadmium complex $[Cd(H_2O)_5L]^+$), two outer sphere acidic anions and two molecules of water of crystallisation. The analysis of DTA shows that complexes of Mn,Zn,Cd with high water content at 35-55°C are transformed to hydrate isomers:

$$[M(H_2O)_6]L_2\cdot 2H_2O \xrightarrow{50-55^\circ} [M(H_2O)_4L_2]4H_2O \quad (M=Mn,Zn)$$

$$[Cd(H_2O)_5L]L\cdot 2H_2O \xrightarrow{35^\circ} [Cd(H_2O)_4L_2]3H_2O.$$

The crystal structure of the complexes obviously indicates that with temperature increase the carboxyl group oxygen replaces two more weakly bonded transoid water molecules($Mn-OH_2$ 2.228(5) Å) from coordination sphere of metal. In this case the COO^-group is coordinated to Mn as a unidentate ligand, the two water molecules is removed from metal coordination transfering in the outer sphere.

The further heating results in dehydration of the complexes with stable anhydrous and small amount of water containing phases formation. In the case of Mn complexes first is formed the stable phase containing three molecules of water/7/. With temperature increase the structural function of acidic anion is changed. If in the initial octahydrate complex the acidic anion is outer sphere, Table. Thermograviometric data for the complexes studied

Complex	Temperature range, °C(DTA)	t_{max}, °C (DTA)	Stable intermediate product existence temperature, °C	Mass loss %		Solid state products composition
				Found	Calc	
$MgL_2{}^8H_2O$	65-140	105(-)	130-135	21.2	20.4	$MgL_2{}^3H_2O$
	140-180	150(-)	160-170	28.6	28.5	$MgL_2{}^2H_2O$
	180-215	195(-)	200-210	32.4	32.6	MgL_2
	215-260	225(-)	250-265	48.9	48.2	Mg_2L_2L'
	260-730			91.7	91.0	MgO
$CoL_2{}^8H_2O$	65-200	85,105,120(-)	150-155	26.8	26.4	CoL_2H_2O
		155(-)	190-205	30.4	30.2	CoL_2
	200-240	215(-)	280-330	43.1	44.6	Co_2L_2L'
	480-710			87.5	87.6	Co
	710-800	720(+),790(+)	815-870	83.8	83.2	Co_3O_4
	850-910	825(-)	890-1000	84.9	84.3	CoO
$NiL_2{}^8H_2O$	60-235	80,105,120,170	145-170	28.3	30.2	NiL_2
	235-290	250(-)	290	57.4	59.2	NiL'
	310-645		645	88.7	87.7	Ni
	645-745	680(+)	775-1000	85.3	84.3	NiO
$ZnL_2{}^8H_2O$	35-60	55(-)				$ZnL_2{}^8H_2O$
	60-175	105(-)	130-185	29.3	29.8	ZnL_2
	175-215	185(-)	melting			ZnL_2
	215-265	235(-)	310-360	45.2	44.1	Zn_2L_2L'
	395-905		895-1000	83.2	83.2	ZnO
$MnL_2{}^8H_2O$	35-70	50(-)				$MnL_2{}^8H_2O$
	70-130	150(-)		18.3	19.0	$MnL_2{}^3H_2O$
	130-210	135(-)	160-175	27.6	26.6	MnL_2 H_2O
		190(-)	210-240	29.6	30.4	MnL_2
	250-310	280(-)	310-370	60.4	59.4	MnL'
	370-705			85.7	83.9	Mn_3O_4
$CdL_2{}^7H_2O$	25-50	35(-)				$CdL_2{}^7H_2O$
	50-185	85(-)	120-255	25.4	24.6	CdL_2
	275-345	315(-)	335-370	50.8	51.4	CdL'
	345-915		890-1000	76.0	75 0	CdO

then after the hydrate isomerisation it coordinates to Mn as unidentat ligand, while after the remove of 5 molecules of water the carboxylic group manifests itself as bridging bidentate ligand.

In the anhydrous and monohydrate crystals apparently the acidic anion performs the more complex polydentate structural function or the coordination number of Mn is decreased to 4-5, its bidentate-bridging function of COO group remaining.

In the Table there are given the main thermographic data for the studied complexes. The analysis of thermograviograms indicates that the temperatures of the dehydration start of isostructural complexes factually do not distinguish from each other and are in temperature range 60-70°C. However the process of full dehydration, as well as the number of stages for each complex depending upon the metal nature are different. The decomposition of anhydrous complexes proceeds with the isolation of p-hydroxybensoic acid, formation of stable intermediate products of ML' and M_2L_2L' composition: $ML_2 \xrightarrow{250-315^\circ} ML' + HL$ (M=Mn,Cd,Ni; $L' = OC_6H_4COO^{2-}$)

$$2ML_2 \xrightarrow{215-235^\circ} M_2L_2L' + HL \quad (M=Mg,Co,Zn).$$

Afterwards there proceeds the crystallisation and rearrangement of intermediate compounds such as ML' and M_2L_2L' with their subsequent destruction. These complex processes are stated on the DTA curves with the corresponding endo- and exothermic effects. The final results of thermolysis are the oxides of corresponding metals. Ni and Co complexes are destructed to free metal, its oxidation being the consequent process.

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