Thermochimica Acta, 93 (1985) 61-64
Elsevier Science Publishers B.V., Amsterdam

THE IR-SPECTRA AND THERMAL DECOMPOSITION OF ARYL-CARBOXYLATES OF ALKALINE-EARTH METALS

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ABSTRACT

IR-spectroscopic and thermogravimetric studies of arylcarboxylates of bivalent Mg, Ca, Sr, Ba had been carried out. The solid phased intermediate and resultant products of thermolysis had been identified. The possible scheme of destruction of the complexes is suggested. By means X-ray and IR-spectral analysis the structure of the complexes had been studied.

INTRODUCTION

The reported data on structure and properties of carboxylates of the alkaline-earth metals are limited /1-4/. The thermal decomposition of formiates /1/ and oxalates /2/ Mg, Ca, Ba had been studied. The crystal structures of p-aminobenzoate and p-oxybenzoate complexes Ba /3/ and Sr /4/ are determined. In the present work there are given the results of IR-spectrascopic and thermogravimetric studies of benzoates, tolidinates and metoxybenzoates of Mg, Ca, Sr, Ba. The preliminary study has showed that the comlexes do have a biological activity.

MEASURING METHODS

Preparation of the complexes. - The complexes was prepared by allowing 1:2 mole proportions of alkaline-earth metal chlorides or nitrates and Na-salt of corresponding acids to react in wate at room temperature, pH of the solution 6-7. The composition of the complexes is determined by the method of element analysis.

Apparatus. - The process of thermal decomposition of the complexes had been investigated in dynamic conditions under air on Hungarian MOM-model at heating rate 10°/min. Al_2O_3 was used as ethalone, Pt crucibles. The X-ray powder analyses had been done on

Proceedings of ICTA 85, Bratislava

Dron-2-model (λ CuKα-radiation, V=32kv, I=20mA). The i.r. spectra of the complexes were recorded by a UR-10 automatic spectrophotometer in the range 4000-800 cm^{-1}. The samples were prepared as KBr pellets.

RESULTS AND DISCUSSION

The X-ray powder analysis had showed that the complexes were the individual crystal compounds. The absence of analogue between the diffraction pictures of complexes excludes their isostructural compounds. However, an arrangement of some analogous diffraction maximums in the field of small angles on the diffracgrams of the dry tolydinates and metoxybenzoates of metals indicates the proximity of their structures. According to the diffractograms these compounds for their structure are close to p-oxybenzoate complexes of barium - $Ba(HOC_6H_4COO)_2 \cdot H_2O$. The crystal structure of $Ba(HOC_6H_4COO)_2 \cdot H_2O$ /3/ is layed, along each side of which are codirectively arranged densely packed and coordinated by the atoms of Ba (through the O atoms of COO group) p-oxybenzoate anions. This kind of structure has to give a value $\sim$ 33-34 Å for the long axe of cell. The indicated value of a parameter is observed both in $Ba(HOC_6H_4COO)_2 \cdot H_2O$ and in the investigated compouds. The high decomposition temperature of complexes, is apparantly connected with their solid polymer structure.

In the Table there are given the main thermographic data for the studied complexes. The dehydratation process and the general character of thermolysis are the same for all compounds. The final products of thermolysis are MgO, CaO, $SrCO_3$, $BaCO_3$.

In i.r. absorption spectra of the complexes, an anty-symmetric and symmetric vibration of COO group have been discovered in the region of 1530-1580 and 1390-1445 cm^{-1}. A decrease of differences between ν_{as} and ν_s vibrations of COO group to the value 100-135 cm^{-1} showed to the bidentate or tridentate-bridged coordination of a carboxylic group with the metal atoms, as in $Ba(HOC_6H_4COO)_2 \cdot H_2O$ /3/. In a spectrum of the benzoate complexes the presence of an absorption bands at about 1700 cm^{-1} testifies to the presence of neutral benzoic acid molecules. The endothermal effects on DTA curves in benzoate complexes at the temperatures 205 (Mg), 210 (Ca), 215 (Sr) and 210°C (Ba) characterize the removal of the free molecule of a benzoic acid arranged in a crustal cell of compounds. The high temperature of dehydration and also

a displacement of valent vibrations of water in the region of less frequency as compared with a free OH-group shows that a part of water molecules is the coordinated.

Table

Dehydration and decomposition temperatures of the complexes

Compounds*	Temperature range, °C	t max. endoeffects, °C	Mass loss,% Found.	Mass loss,% Calc.	Solid State products composition
1	2	3	4	5	6
$MgL_2 \cdot 6LH \cdot 2H_2O$	45-155	70,95	3,7	3,5	$MgL_2 \cdot 6LH$
	180-240	205	74,6	74,3	MgL_2
	395-555	**	95,5	96,1	MgO
$CaL_2 \cdot 0,5LH \cdot 2H_2O$	45-100	90	5,2	4,8	$CaL_2 \cdot 0,5LH \cdot H_2O$
	100-125	105	7,9	7,1	$CaL_2 \cdot 0,5LH \cdot 0,5H_2O$
	125-145	135	9,1	9,5	$CaL_2 \cdot 0,5LH$
	170-230	210	24,2	25,6	CaL_2
	250-575	**	71,3	73,6	$CaCO_3$
	685-770	745	83,9	85,2	CaO
$SrL_2 \cdot 0,5LH \cdot 3H_2O$	85-140	100	3,6	4,0	$SrL_2 \cdot 0,5LH \cdot 2H_2O$
	140-185	170	11,7	12,1	$SrL_2 \cdot 0,5LH$
	190-250	215	24,9	25,8	SrL_2
	305-615	**	65,7	66,7	$SrCO_3$
$BaL_2 \cdot 1,5LH \cdot 0,5H_2O$	40-100	70	1,1	1,6	$BaL_2 \cdot 1,5LH$
	185-225	210	34,0	33,6	BaL_2
	410-650	**	65,9	65,5	$BaCO_3$
$MgL'_2 \cdot 4H_2O$	45-105	90	10,1	9,9	$MgL'_2 \cdot 2H_2O$
	105-185	125	19,1	19,7	MgL'_2
	325-625	**	87,4	89,1	MgO
$CaL'_2 \cdot 3H_2O$	30-120	80	13,1	12,8	$CaL'_2 \cdot 0,5H_2O$
	120-145	130	14,5	14,8	CaL'_2
	240-650	**	73,7	72,5	$CaCO_3$
	690-775	745	86,3	84,6	CaO
$SrL'_2 \cdot H_2O$	120-215	170	4,4	4,8	SrL'_2
	270-665	**	59,6	60,6	$SrCO_3$
$BaL'_2 \cdot 2H_2O$	45-145	90	7,6	8,1	BaL'_2
	305-695	**	54,1	55,5	$BaCO_3$

cont.Table

1	2	3	4	5	6
$MgL''_2 \cdot 4H_2O$	50-100	75	8,3	9,0	$MgL''_2 \cdot 2H_2O$
	100-195	135	17,1	18,1	MgL''_2
	270-565	**	89,9	89,9	MgO
$CaL''_2 \cdot H_2O$	135-230	180	4,8	5,0	CaL''_2
	310-540	**	71,6	72,2	$CaCO_3$
	725-760	740	84,3	84,4	CaO
$SrL''_2 \cdot 1,5H_2O$	105-190	140,160	4,3	4,3	$SrL''_2 \cdot 0,5H_2O$
	190-210	205	6,1	6,5	SrL''_2
	280-490	**	63,2	64,5	$SrCO_3$
BaL''_2	255-450	**	55,3	55,1	$BaCO_3$

* $L=C_6H_5COO^-$; $LH=C_6H_5COOH$; $L'=p\text{-}CH_3C_6H_4COO^-$; $L''=p\text{-}CH_3OC_6H_4COO^-$

** In the given temperature interval a complex process of decomposition of the arid compounds, being accompanied on the DTA curve, overlaying each-other by endo- and exothermal effects, is proceeding.

REFERENCES

1 Baraldi P. Spectrochimica Acta, 35A (1979) 1003
2 Fabbri G., Baraldi P. Atti Soc. Mat. di Modena, 106 (1975) 57
3 Shnulin A.N., Nadjafov H.N., Mamedov Kh.S., Zh. Struckt. Khim., 25 (1984) 89
4 Amiraslanov I.R., Musayev F.N., Mamedov Kh.S., Zh. Struckt. Khim., 23 (1982) 114