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STUDIES OF THERMAL DECOMPOSITION OF BISSALICYLOALDOXIMATES OF SOME HEAVY METALS

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ABSTRACT

Decomposition of zinc, cadmium, lead and mercury bissalicyloaldoximates has been examined by TG, DTG and DTA methods. Elementary analysis, analysis of IR spectra and X-ray radiography of the sinters has been made. Thermal decomposition reaction of the compounds under investigation has been suggested. Where possible, computer calculations of the mechanism and associated kinetic data using the integral method, have been made.

INTRODUCTION

Salicyloaldoxime forms sparingly soluble mono - and bis - compounds with ions of bivalent metals[1]. Bis compounds exhibit an intracomplex salt character.
A stable six-membered ring results from the formation of a bond between the metal ion and oxygen of the hydroxyl group and nitrogen of the oxime group.

In the present work, thermal decomposition of zinc, cadmium, lead and mercury has been investigated. It is a continuation of thermal analyses of compounds exhibiting intracomplex salt character[2].

EXPERIMENTAL

All analytically pure reagents produced by POCh-Gliwice were used without further purification. Salicyloaldoximates were obtained according to the preparation method presented by Lumme and Knuuttile[1]. Thermal analysis was carried out by means of

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OD-102 /MOM Budapest/ derivatograph, temperature range 20-1000°, heating rate 5°/min in air. Sample mass was 50 mg and α - Al_2O_3 was used as reference material. Temperatures at which sinters are obtained and mass losses in individual decomposition stages were determined from TG curves. Elementary analysis of the sinters was made /Table 1/. As an example, Fig. 1 presents thermal analysis curves for mercury and zinc, salicyloaldoximates.

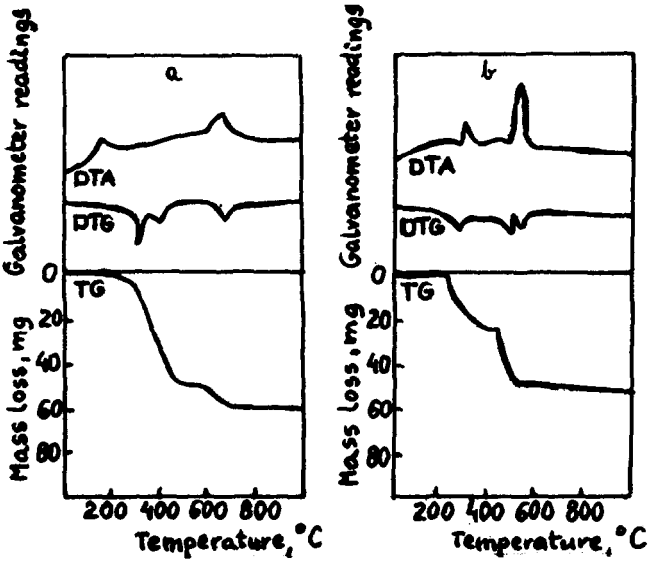

Fig. 1 Thermal analysis curves: a/ mercury salicyloaldoximate b/ zinc salicyloaldoximate

IR spectra of the compounds before heating and of their sinters were analysed. IR spectra were recorded in the range of 4500 - 400 cm^{-1}. The sinters were prepared in the form of tablets in KBr.

Diffractometric examination of the sinters was carried out by means of DRON-1 diffractometer, using Cu-K_α radiation with nickel filter.

RESULTS AND DISCUSSION

Analysis of TG and DTG curves of the examined compounds indicates that decomposition of zinc and cadmium salicyloaldoximates is a two-stage, and of mercury and lead a three - stage process. Decomposition of zinc compound begins at 165°, and ends at 420°. In the first stage, one molecule of salicyloaldoxime is released and a mono compound is formed /Table 1 , IR analysis/. In the se-

Table 1. Characteristic of sinters of salicyloaldoximates under investigation

Complex	Temperature Range [°C]	Resulting compound formula	Calculated [%]					Found [%]				
			mass loss [%]	C	H	N	M	Mass loss [%]	C	H	N	M
$Zn(C_7H_6O_2N)_2$	165-300	$Zn(C_7H_5O_2N)$	40,6	41,1	2,5	6,9	32,5	39,9	41,5	2,9	7,0	32,2
	300-420	ZnO	75,9				80,3	77,9				80,3
$Cd(C_7H_6O_2N)_2$	140-235	$Cd(C_7H_5O_2N)$	35,7	34,0	2,0	5,7	45,2	36,0	34,0	2,1	5,7	45,3
	330-420	CdO	68,2				87,5	68,0				87,6
$Pb(C_7H_6O_2N)_2$	160-220	$Pb(C_7H_5O_2N)$	28,6	24,6	1,5	4,1	60,2	28,0	24,7	1,6	4,1	60,2
	260-280	$(NmC_7H_4OPb)_2O$	30,0	25,2	1,2	4,2	62,7	31,0	25,2	1,4	4,4	63,0
	330-490	PbO	53,4				92,7	54,0				93,0
$Hg(C_7H_6O_2N)_2$	160-	$Hg(C_7H_5O_2N)$	29,0	25,2	1,5	4,2	59,4	30,0	25,4	1,6	4,3	59,0
	-390	solid decomposition products of organic fragment										
	470-580	sample volatilizes										

cond stage the remaining ligand molecule is released and zinc oxide is formed /Table 1 , diffraction pattern/. Changes on the TG curve correspond with four peaks on the DTA curve /Fig. 1/. Decomposition of the cadmium compound begins at 140°. The first stage ends at 235°, and then, up to 330° a slow loss in mass occurs two steps. The sinter obtained at 240° exhibits 36 % mass loss, which corresponds with the release of one ligand molecule /Table 1, IR analysis/. The second rapid change begins at 340° and ends at 420° Cadmium oxide is formed /Table 1, diffraction pattern/.
Decomposition of lead salicyloaldoximate proceeds in three stages. The observed mass losses, elementary analysis of sinters, diffractometric analysis, and IR spectra indicate that in the first stage one ligand molecule is released. In the second stage, as a result of release of one molecule of water from two molecules of monosalicyloaldoximate, a dimer is formed. The final decomposition product is lead oxide. Three exothermic peaks 180°, 285°, 480° occur in the DTA curve. Decomposition of mercury complex begins at 160° /Fig. 1/. The first two stages overlap to a great extent /inflection of the TG curve corresponds with 30 % mass loss and the peak in the DTG curve at 265°/.
Analysis of the sinter obtained at 265° demonstrated that a monocompound is formed /stage I/. The compound immediately decomposes and mercury and a part of organic fragment volatilize /stage II/. The remaining solid of the organic fragment volatilizes in the third stage.

CONCLUSIONS

The following decomposition reactions were suggested: zinc and cadmium salicyloaldoximates /M=Zn, Cd/:

$$\text{I}\quad M\left(C_7H_6O_2N\right)_2 \longrightarrow M\left(C_7H_5O_2N\right) + \uparrow C_7H_7O_2N$$

$$\text{II}\quad M\left(C_7H_5O_2N\right) \longrightarrow MO + \uparrow \text{gaseous decomposition products}$$

Lead salicyloaldoximate:

$$\text{I}\quad Pb\left(C_7H_6O_2N\right)_2 \longrightarrow Pb\left(C_7H_5O_2N\right) + \uparrow C_7H_7O_2N$$

$$\text{II}\quad 2Pb\left(C_7H_5O_2N\right) \longrightarrow H_2O + \left(N{\equiv}C\text{-}C_6H_4\text{-}OPb\right)_2O$$

III $\left(N{\equiv}C\text{-}C_6H_4\text{-}OPb\right)_2O \longrightarrow PbO + \uparrow$gaseous decomposition products.

Mercury salicyloaldoximate

I $Hg\left(C_7H_6O_2N\right)_2 \longrightarrow Hg\left(C_7H_5O_2N\right) + \uparrow C_7H_7O_2N$

II $Hg\left(C_7H_5O_2N\right) \longrightarrow A^{*} + \uparrow$gaseous decomposition products

III $A \longrightarrow \uparrow$gaseous decomposition products

(A^{*} - solid products of organic fragment decomposition)

Applying the case model approach and making use of a computer, the mechanism and kinetic parameters of the first decomposition reaction of cadmium and lead compounds were determined.

The following parameters were obtained for the cadmium compound: the decomposition proceeds according to mechanism A5

$$E = 12{,}1 \text{ kcal/mole}, \quad A = 5{,}7 \cdot 10^4, \quad \sigma = 0{,}071$$

For lead compound - mechanism A2

$$E = 14{,}6 \text{ kcal/mole}, \quad A = 6 \cdot 10^5, \quad \sigma = 0{,}024$$

It was impossible to determine parameters for the reaction of the first decomposition stage of the zinc complex. In the course of the change, a strong absorption decomposition products probably occurs, resulting in slower mass loss and in a different shape of the TG curve /Fig. 1/.

REFERENCES

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