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THERMAL DECOMPOSITIONS OF ZINC(II) BENZENEDICARBOXYLATES

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The thermal decompositions of zinc(II)benzenedicarboxylates were studied in air atmosphere at a heating-rate of 10 deg $\min^{-1}$. Zinc phthalate and isophthalate were dehydrated in one step and next decomposed directly to ZnO. Zinc terephthalate was dehydrated in two steps and then decomposed directly to ZnO.

Metal complexes with benzenedicarboxylic acids are little known. In recent years we have studied the thermal decompositions of benzenedicarboxylates of some transition metals: scandium(III) [1], zirconium(IV) [2] and copper(II) [3]. As a continuation of our work on the thermal decompositions of carboxylates of transition [4] and inner transition elements [5–6], we now report the thermal decompositions of zinc(II) benzenedicarboxylates in air atmosphere.

Experimental

Zinc(II) phthalate, isophthalate and therephthalate were prepared by adding a 0.1 *M* solution of ammonium benzenedicarboxylate to a hot 0.2 *M* solution of zinc nitrate (pH 4.5–5.0). The precipitate formed was heated in the mother liquor for 0.5 h on a water bath at 333–343 K, filtered off, washed with water to remove NH_4^+, and dried at 303 K to constant mass.

The contents of carbon and hydrogen in the zinc benzenedicarboxylates were determined by elemental analysis by using V_2O_5 as oxidizing agent. The zinc contents were determined by ignition of the complexes to ZnO at 1173 K. The water contents were determined from the TG curves and by isothermal heating of the complexes at a definite temperature.

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In order to confirm the chemical compositions of the obtained salts, their IR spectra and the spectra of the benzenedicarboxylic acids were recorded over the range 4000–400 cm^{-1} with a UR–20 spectrophotometer. The results are given in Table 1. The diffractograms of the prepared complexes were recorded with a DRON–2 diffractometer.

Table 1 Analytical data

Complex	Zn, %		C, %		H, %	
	calcd.	found	calcd.	found	calcd.	found
ZnL* · $1.5H_2O$ (1, 2)	25.48	25.67	37.42	37.46	2.14	1.97
ZnL · $2H_2O$ (1, 3)	24.62	24.71	36.15	35.93	3.03	2.94
ZnL · $3.5H_2O$ (1, 4)	22.35	22.10	32.82	32.52	3.80	4.14

* L = $C_6H_4(COO)_2^{2-}$;
(1, 2), (1, 3), (1, 4) = positions of COO^- groups

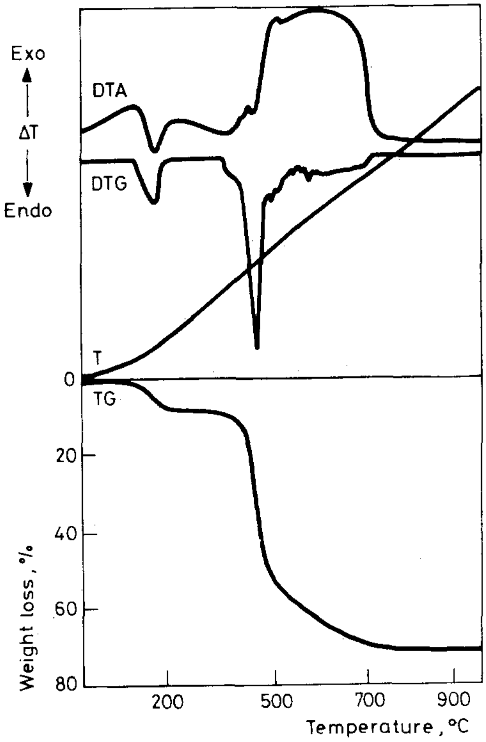

Fig. 1 TG, DTG and DTA curves of zinc(II) phthalate hydrate

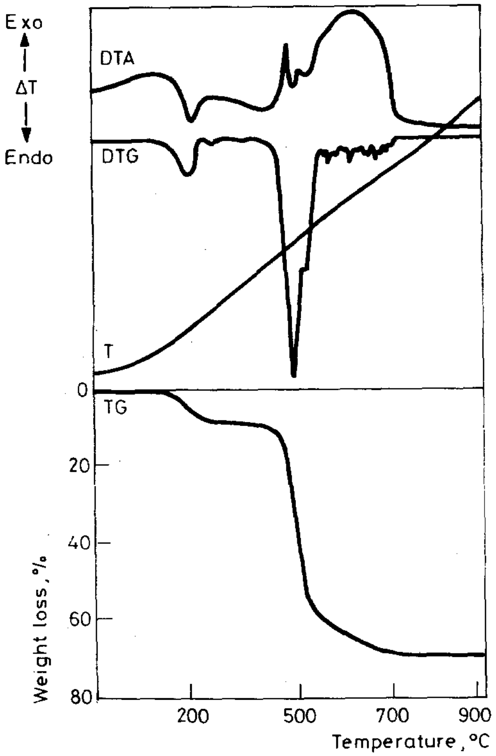

Fig. 2 TG, DTG and DTA curves of zinc(II) isophthalate hydrate

The thermal stabilities of the prepared complexes were studied by means of TG, DTG and DTA techniques. The measurements were made with a derivatograph at a heating rate of 10 deg min^{-1}. The samples were heated in ceramic crucibles in air atmosphere. The results are presented in Figs 1–3 and Table 1.

Results and discussion

Zinc(II) phthalate, isophthalate and terephthalate were prepared as white crystalline solids, sparingly soluble in water. They are characterized by low symmetry and a large unit cell. The complexes are hydrated with various degrees of hydration, and with a molar ratio of metal to ligand of 1 : 1 (Table 1).

Analysis of the IR spectra of the prepared complexes confirms their formulation. In the IR spectra of zinc phthalate, isophthalate and terephthalate, there are broad absorption bands with maximum at 3260–3200 cm^{-1} and a sharp band at 1630–1600 cm^{-1}, which indicate the presence of crystallization water molecules,

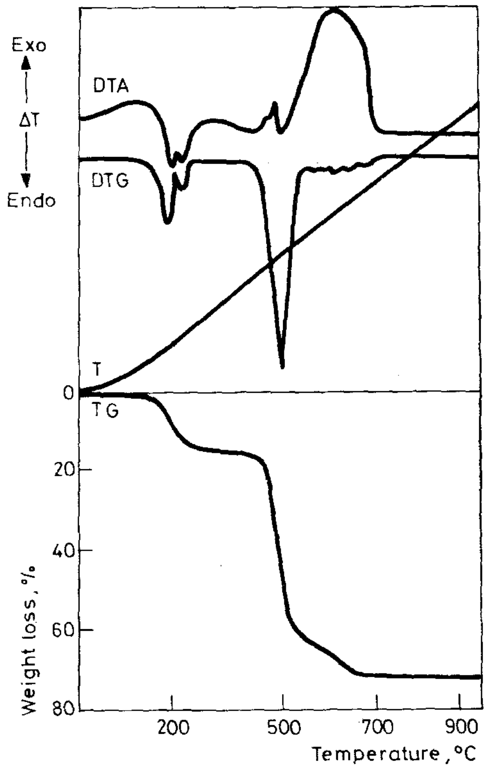

Fig. 3 TG, DTG and DTA curves of zinc(II) terephthalate hydrate

absorption bands at 1580–1530 cm^{-1} anf 1410–1390 cm^{-1} due to asymmetric (ν_{as}) and symmetric (ν_s) vibrations of the COO$^-$ ion (Table 2) and bands at 530–450 cm^{-1} due to the Zn—O bonds.

The magnitude of separaton of the asymmetric and symmetric bands (ν_{as}–ν_s) of the COO$^-$ group increases in the sequence: iso-

Table 2 Frequencies of absorption bands of COO$^-$ group [cm^{-1}]

Compound		$\nu_{C=O}$	ν_{as} COO$^-$	$\Delta\nu_{as}$	ν_s COO$^-$	$\Delta\nu_s$	ν_{as}–ν_s	Zn—O
$C_6H_4(COOH)_2$	(1.2)	1685	1580	—	1400	—	180	—
$ZnL \cdot 1.5H_2O$	(1.2)	—	1530	50	1390	10	140	455
$C_6H_4(COO)_2$	(1.3)	1690	1580	—	1920	—	160	—
$ZnL \cdot 2H_2O$	(1.3)	—	1540	40	1410	10	130	475
$C_6H_4(COO)_2$	(1.4)	1690	1570	—	1420	—	150	—
$ZnL \cdot 3.5H_2O$	(1.4)	—	1580	10	1400	10	180	530

Table 3 Data on thermal decompositions of zinc(II) *o*-, *m*- and *p*-phthalates

Complex		ΔT_1	Loss in weight,%		n, H_2O	Endo-effect, T	ΔT_2	T_{max}	Loss in weight, %		T_k	Decomposition effects, T	
			calcd.	found					calcd.	found		endo	exo
ZnL · 1.5	(1.2)	393–453	7.02	7.0	1	443	613–993	703	68.27	68.0	993	653	893
ZnL · $2H_2O$	(1.3)	383–493	6.79	7.5	1	483	663–983	753	69.35	69.0	983	643	903
ZnL · $3.5H_2O$	(1.4)	393–483	12.30	11.5	2	473	683–993	768	72.17	72.0	993	673	963
		483–513	15.40	14.5	0.5	513							

ΔT_1 = temperature range of dehydration,
ΔT_2 = temperature range of decomposition to ZnO,
T_{max} = temperature corresponding to maximum loss in weight in TG curve,
T_k = temperature of ZnO formation

phthalate < phthalate < terephthalate, which indicates the increasing ionic bond participation in the complexes. This is a result of the change in position of the COO^- group in the benzene ring and of the changes in the steric and induction effects and the different symmetries of the complex molecules. The $C=O$ band at 1690–1685 cm^{-1} in the IR spectra of the benzenedicarboxylic acids does not appear in the spectra of the complexes, which indicates the absence of the COOH group.

In the spectra of these complexes, the vibrations of Zn—O are not pure ones on account of conjugation of the C—O and C—C group vibrations. The frequency of the absorption bands of the Zn—O vibrations increases with increasing distance between the carboxylic groups in the benzene ring, which indicates the increasing bond stability.

Zinc phthalate probably exists as a dimer, $Zn_2L_2 \cdot 3H_2O$, whereas the isophthalate and terephthalate form polynuclear complexes and the zinc ions are bonded through benzenedicarboxylate ions. Zinc terephthalate has a chain structure due to the para position of the COO^- groups.

When heated the benzenedicarboxylates of zinc decompose in two or three steps. Zinc phthalate and isophthalate (Figs 1–3, Table 3) lose one molecule of crystallization water endothermally when heated, and next the phthalate hemihydrate and the isophthalate monohydrate decompose directly to ZnO over the range 613–993 K. Zinc terephthalate is dehydrated in two steps to the accompaniment of two endothermic effects, and the monohydrate, then decomposes directly to ZnO at 683–993 K. The crystallization water molecules lost endothermally at 393–513 K are probably outer sphere water, whereas the water molecules lost during the decomposition process are inner sphere ones. The decomposition of the complexes is accompained by an endothermic effect, and the combustion of the organic ligand and carbon deflagration by an exothermic one. The most stable complex is zinc terephthalate, which decomposes at 683 K. This fact confirms the results obtained on the basis of the IR spectra. The final product of decomposition of all zinc benzenedicarboxylates is ZnO, which forms at 983–993 K.

References

1 W. Brzyska and R. Kurpiel, Ann. Univ. M. Curie Skłodowska,.Lublin, Polonia, sec. AA 33 (1978) 91.

2 W. Brzyska and P. Sadowski, Pol. J. of Chem., 58 (1984) 669.

3 W. Brzyska and W. Wołodkiewicz, J. Thermal Anal., 34 (1988) 1207.

4 W. Brzyska, R. Kurpiel-Gorgol and M. Dąbkowska, J. Thermal Anal., 28 (1983) 531.

5 W. Brzyska and H. Hubicka, J. Thermal Anal., 31 (1986) 333.

6 W. Brzyska and A. Kula, J. Thermal Anal., 25 (1982) 531.

Zusammenfassung — Bei einer Aufheizgeschwindigkeit von 10°·min^{-1} wurde die thermische Zersetzung von Zink(II)benzoldikarboxylat in Luft untersucht. Zinkphtalat und -isophtalat wird zunächst in einem Schritt dehydratisiert und anschließend zu ZnO zersetzt. Zinkterephtalat wird vor der endgültigen Zersetzung zu ZnO in zwei Schritten dehydratisiert.

Резюме — В воздушной атмосфере при скорости нагрева 10 град/мин изучено термическое разложение бензолдикарбоксилатов цинка. Дегидратация фталата- и изофталата цинка протекает в одну стадию с последующим разложением безводного продукта прямо до окиси цинка. Реакция дегидратации терефталата цинка протекает в две стадии, а образующийся продукт затем разлагается до окиси цинка.