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COMPARATIVE STUDY OF THE THERMAL ANALYSES OF SOME TRANSITION METAL(II) ISO- AND TEREPHTHALATES

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ABSTRACT

The decomposition of iso- and terephthalates of Cu(II) and Zn(II) has been investigated employing simultaneous DTA, TG and DTG. The ultimate thermolysis products are the corresponding metal oxides as confirmed by chemical analysis and X-ray powder diffraction. The TG data for dehydration were computerised to test the various decomposition models. The equation $-\ln(1-\alpha)$ has been found to be the most appropriate in the case of iso- and terephthalates of Cu(II), while $[-\ln(1-\alpha)]^r$ ($r=1/3$) and $\ln(\alpha/1-\alpha)$ are most suitable for iso- and terephthalates of Zn(II), respectively. Comparison of the T_i values led to the stability orders: Zn(tere) > Zn(iso) > Cu(iso) > Cu(tere) and Zn(iso) > Cu(tere) > Cu(iso) > Zn(tere) for dehydration and decomposition processes, respectively.

INTRODUCTION

Although conflicting claims about the reliability of the absolute values of the data from thermal analysis have sometimes been made, the significance of measurements made under similar conditions for comparable compounds has never been questioned. Keeping this in view a comparative study on the thermal decomposition of metal carboxylates has been undertaken. In a previous paper [1] on the thermal analysis of some transition metal propionates different stability orders, i.e., Zn > Co > Cu > Ni and Zn > Co > Ni > Cu, for dehydration and decomposition processes, respectively, have been reported. Such information on thermal stability is very useful for studying the decomposition mechanism. In continuation of that work [1], a comparative study of the thermal decomposition of some more carboxylates (iso- and terephthalates of Cu(II) and Zn(II)) is reported using non-isothermal and simultaneous techniques (DTG, DTA and TG) and X-ray diffraction.

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EXPERIMENTAL

Copper(II) isophthalate dihydrate was prepared by adding small amounts of copper(II) carbonate to the aqueous solution of isophthalic acid in small amounts with constant stirring until the effervescence ceased. The excess of copper carbonate was removed by filtration. The resultant clear solution thus obtained was concentrated on a water bath until crystals appeared. The crystals were filtered off, washed with distilled water and dried in air after recrystallisation. Similarly, the isophthalate of zinc(II) was prepared.

Copper(II) terephthalate monohydrate was prepared by adding copper(II) sulphate pentahydrate solution to the aqueous solution of sodium terephthalate in equimolar proportions. The precipitate of copper(II) terephthalate formed at room temperature was allowed to remain in solution overnight and was then separated by filtration. The precipitate was washed with distilled water a number of times and finally dried in air. The terephthalate of zinc(II) was prepared similarly.

The composition of these compounds was established by chemical analysis and infrared spectroscopy. The percentage of copper and zinc was determined gravimetrically [2]. The percentage of carbon and hydrogen was determined by microanalysis.

The derivatographic study of these compounds was performed on a Paulik–Paulik–Erdey MOM derivatograph (Hungary) using 200 mg (170 mg for copper terephthalate) of the sample at 200 mg sensitivity and at a heating rate of $10^{\circ}\ min^{-1}$ in a static air atmosphere. The X-ray powder diffraction patterns of the end products were recorded using nickel-filtered $Cu K_{\alpha}$ radiation. The computer analysis was performed on a TDC-316 computer (ECIL, India).

RESULTS AND DISCUSSION

Derivatographic study

Non-isothermal study of the iso- and terephthalates of copper(II) and zinc(II) follows.

Copper(II) isophthalate dihydrate

Figure 1 shows the simultaneous DTG, DTA and TG curves of copper(II) isophthalate dihydrate. The DTA curve of this sample shows three endothermic peaks at 418, 495 and 550 K. The endothermic peak at 550 K is followed by an exothermic region from 565 to 913 K. Comparison of DTA and DTG curves shows that all the stages of thermal decomposition are accompanied by weight changes. The TG curve at 565 K shows a weight loss of 13.8% which corresponds to the elimination of two water molecules (calcd. loss =

13.7%). The anhydrous sample then undergoes decomposition without the formation of any intermediate. The TG curve shows a weight loss of 72% at 913 K indicating the formation of CuO (calcd. loss = 69.8%). The end product was confirmed by chemical and X-ray diffraction analysis [3].

Copper(II) terephthalate monohydrate

Figure 2 shows the simultaneous DTG, DTA and TG curves of copper(II) terephthalate monohydrate. The DTA curve shows two broad endothermic peaks at about 333 and 443 K. The endotherms are followed by an exothermic region from 588 to 828 K. There are corresponding peaks in the DTG curve indicating that the thermal effects are accompanied by weight loss. The TG curve shows a weight loss of 6.0% at 588 K indicating the removal of one water molecule. The decomposition of the anhydrous compound is very abrupt and is completed at 873 K. The TG curve at this temperature shows a weight loss of 67% indicating the formation of CuO (calcd. loss = 67.6%). CuO as the final thermolysis product was confirmed by chemical and X-ray diffraction analysis [3].

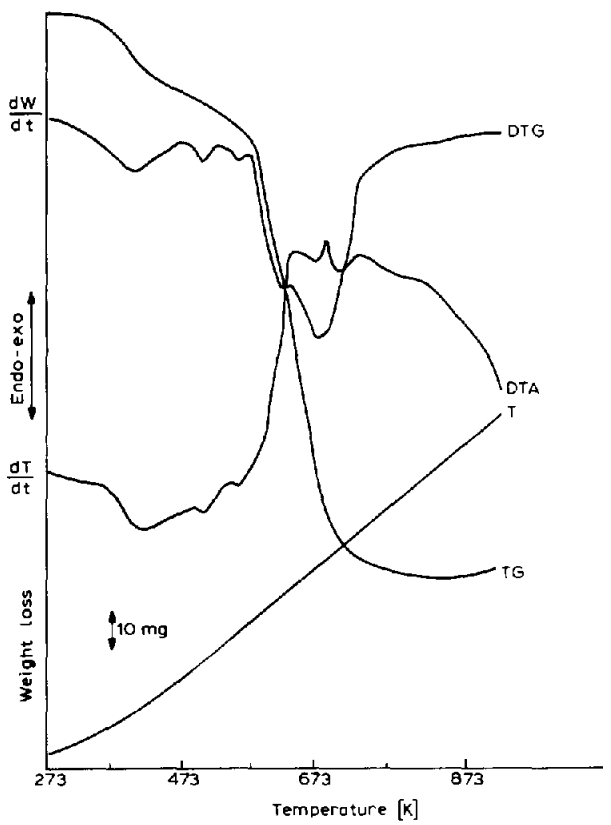

Fig. 1. Simultaneous DTG, DTA and TG curves of copper(II) isophthalate dihydrate at a heating rate of 10° min^{-1}.

Zinc(II) isophthalate dihydrate

Figure 3 shows the simultaneous DTG, DTA and TG curves of zinc(II) isophthalate dihydrate. The DTA curve shows three endothermic peaks at 513, 613 and 653 K; the last peak being immediately followed by an exothermic region between 733 and 993 K. The TG curve shows that the dehydration of this compound takes place in three steps, forming monohydrate at 513 K (weight loss = 7.0%), hemihydrate at 613 K (weight loss = 10.5%) and anhydrous sample at 673 K (weight loss = 12.5%). The TG curve shows the decomposition of the anhydrous sample to be an abrupt process with an arrest at 833 K. A weight loss of 62% at this stage indicates that ZnO_2 may be formed (calcd. loss = 63.4%). Further, a weight loss of 70% at 993 K suggests the formation of ZnO (calcd. loss = 69.4%). The end product as ZnO has been confirmed by chemical analysis and X-ray diffraction [4].

Zinc(II) terephthalate monohydrate

Figure 4 shows the simultaneous DTG, DTA and TG curves of zinc(II) terephthalate monohydrate. In the DTA curve there is an endothermic peak

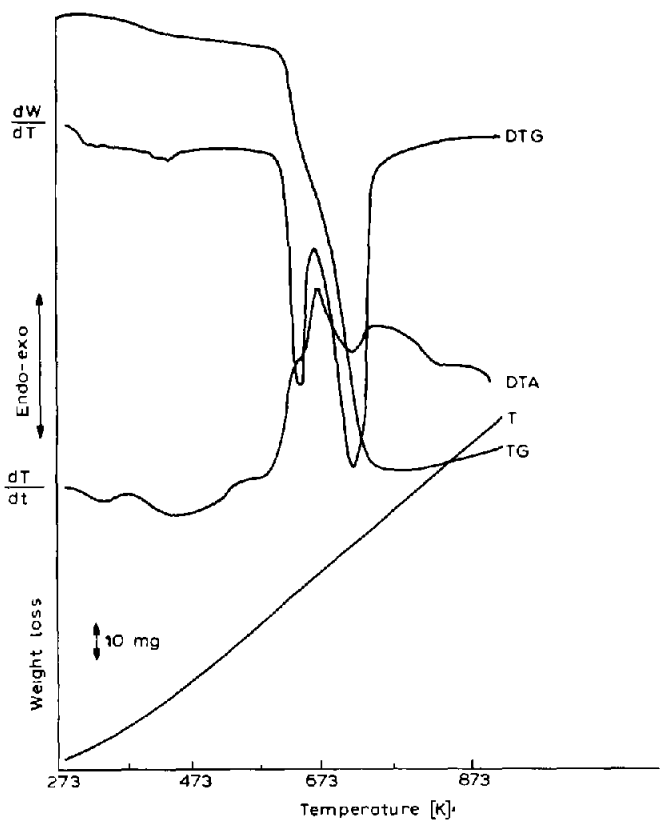

Fig. 2. Simultaneous DTG, DTA and TG curves of copper(II) terephthalate monohydrate at a heating rate of 10° min^{-1}.

at 503 K and an exothermic peak at 683 K. There are corresponding peaks in the DTG curve but at slightly lower temperatures indicating that the thermal changes are accompanied by weight loss. The dehydration of the compound is completed at 528 K as indicated by a weight loss of 8.5% in the TG curve (calcd. loss = 7.3%). From 533 K the decomposition of the sample takes place without any arrest and is completed at 833 K. The TG curve shows a weight loss of 67% at 833 K indicating the formation of ZnO (calcd. loss = 67.1%). The identification of ZnO as the ultimate product has been confirmed by chemical analysis and its X-ray diffraction pattern [4].

Comparative study of the thermal analysis

The derivatographic study shows that the decomposition occurs in stages, dehydration being an endothermic process. Comparison of the T_i values of dehydration (Table 1) shows the stability order: Zn(tere) > Zn(iso) > Cu(iso) > Cu(tere), which is not in agreement with the order obtained from the corresponding T_m values. T_i values always provide a more accurate measure of the thermal stability than do T_m values.

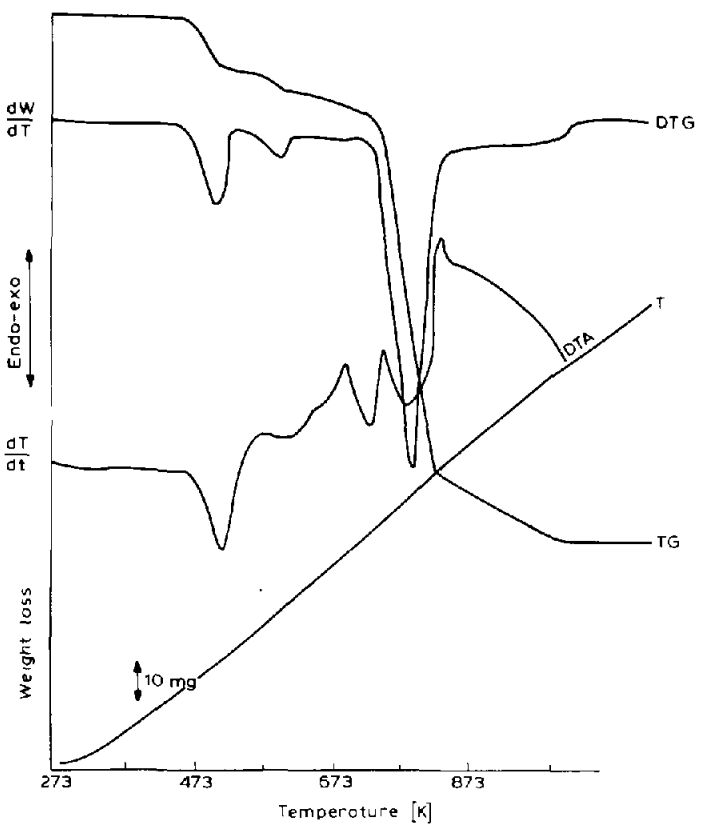

Fig. 3. Simultaneous DTG, DTA and TG curves of zinc(II) isophthalate dihydrate at a heating rate of 10° min^{-1}.

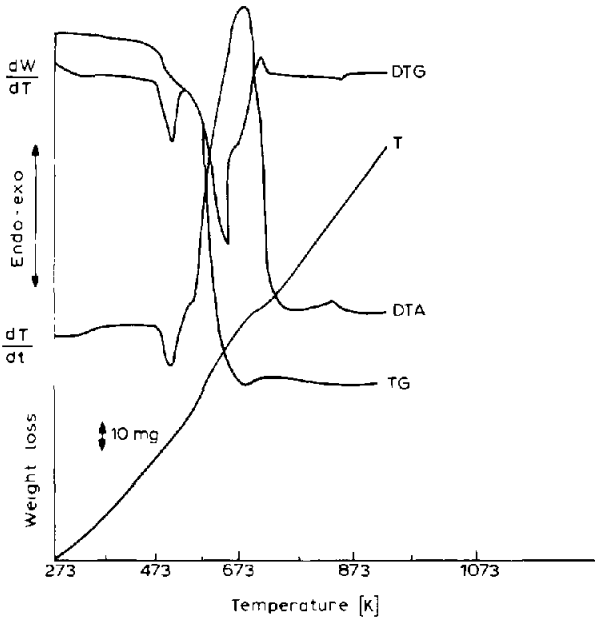

Fig. 4. Simultaneous DTG, DTA and TG curves of zinc(II) terephthalate monohydrate at a heating rate of 10° min $^{-1}$.

The activation energy for the dehydration stage was computed from TG data using the Coats–Redfern equation to which all the known models of decomposition were applied. The computerised kinetic parameters for the dehydration of copper(II) isophthalate dihydrate are given in Table 2. Although the kinetic model No. 6(iii) with $r = 4$ (given in Table 2) provides the lowest chi-square error value, it is not a physically feasible model. The results obtained from the isothermal study of the dehydration of iso- and terephthalates of copper(II) give sufficient evidence for a random-nucleation mechanism for which the equation $-\ln(1-\alpha)$ holds good and also provides reasonable activation energy values (13.64 and 12.16 kcal mol^{-1}, respectively) for dehydration. In the case of zinc(II) isophthalate the Avrami–Erofeev equation, i.e., $[-\ln(1-\alpha)]^r$ with $r = 1/3$, has been found

TABLE 1

T_i and T_m values for the dehydration and decomposition of various transition metal(II) carboxylates

Compound	Dehydration		Decomposition	
	T_i (K)	T_m (K)	T_i (K)	T_m (K)
Iso-Cu($C_8H_4O_4$)·$2H_2O$	353	393	565	613
Tere-Cu($C_8H_4O_4$)·H_2O	343	438	593	633
Iso-Zn($C_8H_4O_4$)·$2H_2O$	463	500	733	790
Tere-Zn($C_8H_4O_4$)·H_2O	478	503	533	653

TABLE 2

Computerised kinetic parameters for the dehydration step in the TG curve of copper(II) isophthalate dihydrate obtained by the Coats–Redfern equation $\log[g(\alpha)/T^2]$ vs. $1/T$, $g(\alpha) = \int_0^{\alpha} d\alpha/f(\alpha)$

Model No.	$g(\alpha)$		Energy, E (kcal mol^{-1})	Pre-exponential factor, Z	Least-sq. error	Chi-sq. error
1	$-\ln(1-\alpha)$		13.64	240.789	0.018	0.090
2 (i)	$-\ln(1-\alpha)^r$	$r=1/4$	0.39	0.011	0.272	0.022
(ii)		$r=1/3$	1.85	0.109	0.366	0.029
(iii)		$r=1/2$	4.78	1.163	0.545	0.044
(iv)		$r=2/3$	7.72	7.769	0.725	0.059
3	$\ln(\alpha/1-\alpha)$		38.23	96.000	0.053	0.577
4	$3[1-(1-\alpha)^{1/3}]$		10.58	33.238	0.846	0.064
5	$2[1-(1-\alpha)^{1/2}]$		9.45	15.504	0.849	0.064
6 (i)	$r-(1-\alpha)^r$	$r=2$	1.26	0.029	0.257	0.022
(ii)		$r=3$	2.31	0.051	0.166	0.014
(iii)		$r=4$	2.77	0.067	0.129	0.011
7 (i)	α^r	$r=1/4$	1.18	0.014	0.265	0.021
(ii)		$r=1/3$	0.25	0.004	0.339	0.027
(iii)		$r=1/2$	1.58	0.060	0.487	0.038
(iv)		$r=1$	6.95	2.636	0.035	0.070
(v)		$r=3/2$	12.17	42.337	0.013	0.991
(vi)		$r=2$	17.26	518.718	0.018	0.125
8	$3/2[1-(1+\alpha)^{1/3}]^2$		24.85	10038.51	0.016	0.106
9	$3/2[(1+\alpha)^{1/3}-1]^2$		15.30	21.32	0.018	0.108
10	$3/2[1-3/2\alpha-(1-\alpha)]^{3/2}$		21.61	1366.207	0.016	0.103
11	$(1-\alpha)\ln(1-\alpha)+\alpha$		21.12	1635.879	0.017	0.114
12 (i)	$\ln \alpha^r$	$r=1$	23.21	0.000	0.046	0.312
(ii)		$r=2$	23.06	0.000	0.046	0.328

to be the most appropriate and physically feasible (activation energy being 35.86 kcal mol^{-1}). However, for the dehydration of zinc(II) terephthalate the Prout–Tompkin equation, i.e., $\ln(\alpha/1-\alpha)$ with activation energy of 31.64 kcal mol^{-1}, has been found to be the most suitable. On the basis of activation energy considerations, the order of thermal stability observed is: Zn(iso) > Zn(tere) > Cu(iso) > Cu(tere).

For decomposition, comparison of T_i values (Table 1) shows the order of thermal stability as Zn(iso) > Cu(tere) > Cu(iso) > Zn(tere).

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