THERMAL STUDIES ON MAGNESIUM, BARIUM AND LEAD ZIRCONYL OXALATES

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ABSTRACT

Magnesium, barium and lead zirconyl oxalates (abbreviated as MZO, BZO and LZO, respectively) have been prepared in aqueous medium. These compounds have been characterized on the basis of elemental analysis and IR spectral studies. The thermal behaviour of these compounds has been studied with the aid of TG, DTG and DSC techniques. The graphical method of Coats and Redfern has been employed to calculate the kinetic parameters such as apparent activation energy and order of reaction. Heats of reaction for different decomposition steps have been calculated from the DSC curves. The intermediates obtained at the end of various thermal decomposition steps were identified on the basis of elemental analysis and IR spectral studies.

INTRODUCTION

It has been known for a long time that early transition metals, especially titanium and zirconium, form an extensive series of compounds called titanates and zirconates in which titanium and zirconium play the role of acidic constituents. Owing to the possession of desirable dielectric and piezoelectric properties [1], the titanates/zirconates have found extensive use in various electrical devices. The importance of bivalent metal titanyl/zirconyl oxalates lies in the fact that these compounds yield bivalent metal titanates/zirconates on ignition at higher temperatures. In recent years, a large number of bivalent metal titanates/zirconates have been studied [1—12]. Though Sheinkman et al. [12] have studied the thermal decomposition of barium zirconyl oxalate, we have restudied this compound. However, there is no report in the literature on magnesium and lead zirconyl oxalates.

EXPERIMENTAL

All the reagents used for the preparation of these compounds were either BDH, Analar or E. Merk "Proanalysi grade".

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Preparation of the compounds

Barium zirconyl oxalate was prepared using a method similar to that described for barium titanyl oxalate by Clabaugh et al. [1]. For preparing the magnesium and lead zirconyl oxalates, the above method required some modifications, as reported for the preparation of the corresponding titanyl oxalates of these bivalent metals [7, 10, 11].

Analysis

Estimations of the carbon and hydrogen contents were carried out in our departmental microanalytical laboratory. The bivalent metals and zirconium contents were determined by standard methods [13].

Physical measurements

Infrared spectra of these compounds were recorded in KBr medium in the region 4000—200 cm^{-1} using a Perkin Elmer-621 grating spectrophotometer.

TG and DTG were recorded simultaneously on a "Setaram G-70" thermo-analyzer, Lyon, France, with a sample size of 26—36 mg, heating rate of 8 K min^{-1} and a flow rate of gas of 10 ml min^{-1}. The DSC curves were recorded using a Perkin-Elmer differential scanning calorimeter Model DSC-1 in the temperature range 273—773 K in an atmosphere of nitrogen.

RESULTS AND DISCUSSION

The methods used for the preparation and isolation of these compounds yield materials of high purity, as can be judged by satisfactory elemental analysis, IR spectra and thermoanalytical data. All the compounds are obtained in crystalline form. These are insoluble in water and common organic solvents, e.g. methanol, ethanol, benzene, acetone, ether and chloroform, etc. They are quite stable as solids in air for a long time.

IR spectral studies

The IR spectra of these compounds have been discussed on the basis of the empirical band assignments for the free oxalato anion [14].

In general, lattice water absorbs at 3550—3200 cm^{-1} (antisymmetric and symmetric OH stretching) and at 1632—1600 cm^{-1} (HOH bending), although these compounds absorb clearly near 3300 cm^{-1} which can be assigned to OH stretching vibrations. But the HOH bending vibration seems to be merged with asymmetric C=O vibrations which appear in the range 1650—1750 cm^{-1}. Further, a series of coupled vibrations have been observed in these compounds around ~1400 cm^{-1}, ~1350 cm^{-1}, ~900 cm^{-1}, ~800 cm^{-1}, ~520 cm^{-1}, ~500 cm^{-1} and ~400 cm^{-1}, which may be assigned to ν(C—O) + ν(C—C), ν(C—O) + δ(O—C=O), ν(C—O) + ν(Zr—O) + δ(O—C=O), δ(O—C=O) + ν(Zr—O), ν(C—C) + ν(Zr—O), ring deformation + δ(O—C=O) and ν(Zr—O) + ring deformation, respectively [15].
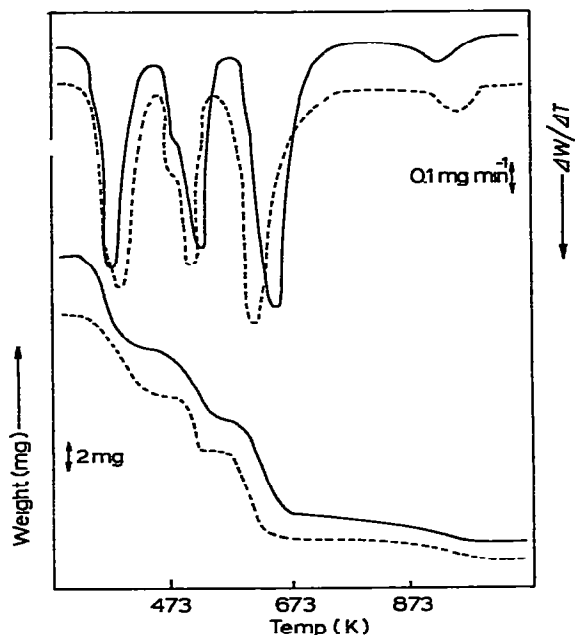
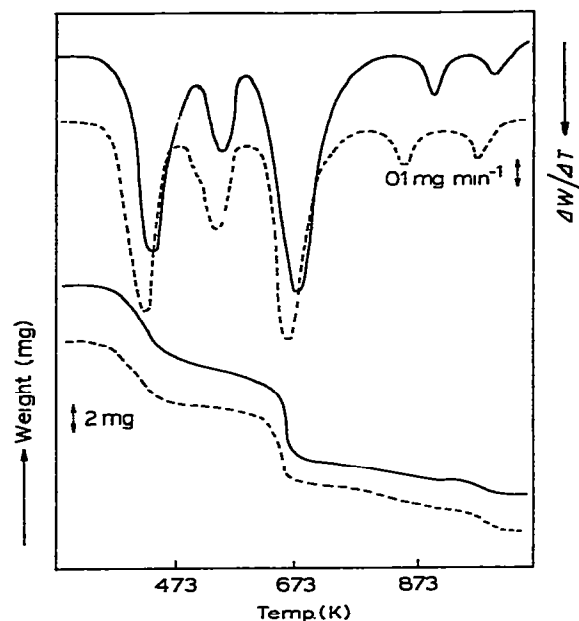Fig. 1. TG and DTG curves of MZO. ———, In N_2; — — —, in O_2.

Fig. 2. TG and DTG curves of BZO. ———, In N_2; — — —, in O_2.

Thermal analysis

Figures 1—3 present the TG and DTG curves of MZO, BZO and LZO, respectively, in dynamic atmospheres of nitrogen and oxygen, and Fig. 4 incorporates the DSC curves of MZO, BZO and LZO in nitrogen atmosphere only.
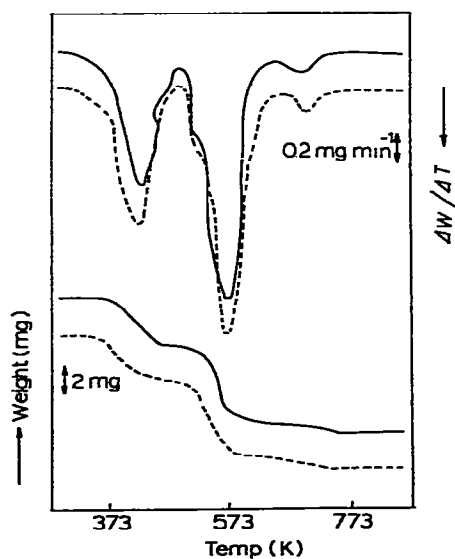

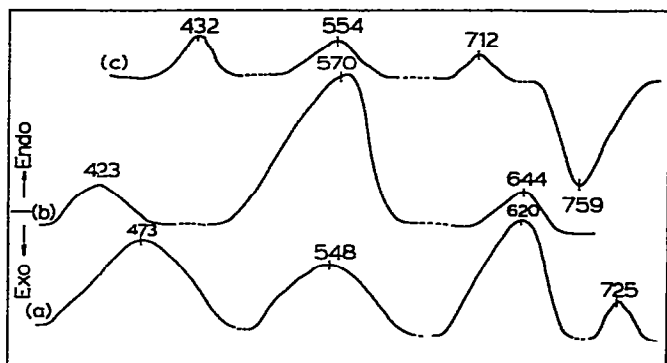Fig. 3. TG and DTG curves of LZO. ———, In N_2; — — —, in O_2.

Fig. 4. DSC curves of oxalates. (a) MZO; (b) BZO, (c) LZO.

It is evident that the thermal behaviour of these compounds consists of three major changes, viz. the dehydration of the hydrated compounds, the decomposition of the oxalates to the respective carbonates, and finally the decomposition of the carbonates to the respective metal zirconates. These steps are not significantly influenced by the surrounding gaseous atmospheres employed.

Dehydration of the hydrated compounds

MZO becomes completely dehydrated in the temperature range 298—523 K. The observed weight loss in the above temperature range corresponds to seven molecules of water of crystallization. The dehydration of BZO and LZO occurs in the temperature ranges 333—473 K and 303—463 K, respectively. The observed weight losses in the temperature range mentioned above are indicative of the tetrahydrate nature of these two compounds. The expected endothermic behaviour for the dehydration process associated with these compounds has been observed from DSC curves in almost the same temperature ranges.

Decomposition of the dehydrated oxalates

The decomposition of MZO and BZO to the respective carbonates takes place in two consecutive steps. In the first step, oxalate groups are partly decomposed to the carbonate, resulting in the formation of an oxalato—carbonate complex, which further decomposes in the second step to give the respective carbonates; while in the case of LZO, decomposition of the dehydrated oxalate to the carbonate is completed only in a single step.

The residue obtained after the first step endothermic decomposition of anhydrous magnesium zirconyl oxalate has been assigned to composition $Mg_2Zr_2O_4(C_2O_4)CO_3$ on the basis of its weight loss, elemental analysis and IR spectral studies. Further decomposition of this intermediate, which is also endothermic in nature, results in the formation of the pure carbonate, $Mg_2Zr_2O_5CO_3$, as evidenced by its weight loss, elemental analysis and IR bands. However, in the case of anhydrous barium zirconyl oxalate, the first step endothermic decompositon results in the formation of an intermediate, $Ba_2Zr_2O_2(C_2O_4)_3CO_3$, as evidenced by its elemental analysis and IR spectral data. The consecutive endothermic decomposition of this intermediate

results in the formation of the pure carbonate, $Ba_2Zr_2O_5CO_3(CO_2)$. The presence of entrapped carbon dioxide has been supported by an IR spectral band near 2350 cm^{-1}. The thermal decomposition of dehydrated lead zirconyl oxalate to its respective carbonate takes place in a single endothermic step.

Decomposition of the carbonates

$Mg_2Zr_2O_5CO_3$ decomposes between 673 and 748 K to produce magnesium zirconate ($MgZrO_3$). The carbonate, $Ba_2Zr_2O_5CO_3(CO_2)$, decomposes in two well-defined steps. In the temperature range 593—933 K the release of entrapped CO_2 occurs to give the carbon dioxide free carbonate, $Ba_2Zr_2O_5$-CO_3. This further decomposes between 943 and 1023 K to give the final decomposition product, barium zirconate ($BaZrO_3$); while the carbonate Pb_2-$Zr_2O_5CO_3$ decomposes in a single step to give lead zirconate ($PbZrO_3$) between 603 and 743 K. The corresponding DSC curves showed the decomposition of the carbonates to their respective oxides to be endothermic in nature, but for LZO the initial reaction is endothermic followed by an exothermic reaction. This is probably due to the transition of one crystalline form of $PbZrO_3$ to another.

From the above results, schemes I, II and III may be proposed for the decomposition of MZO, BZO, and PZO, respectively, in an atmosphere of nitrogen.
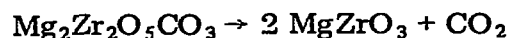
Scheme I

Step I: dehydration

$MgZrO(C_2O_4)_2 \cdot 7\ H_2O \rightarrow MgZrO(C_2O_4)_2 + 7\ H_2O$

Step II: initial oxalate decomposition

$2\ MgZrO(C_2O_4)_2 \rightarrow Mg_2Zr_2O_4(C_2O_4)CO_3 + 3\ CO + 2\ CO_2$

Step III: final oxalate decomposition

$Mg_2Zr_2O_4(C_2O_4)CO_3 \rightarrow Mg_2Zr_2O_5CO_3 + CO + CO_2$

Step IV: decomposition of carbonate

$Mg_2Zr_2O_5CO_3 \rightarrow 2\ MgZrO_3 + CO_2$

Scheme II

Step I: dehydration
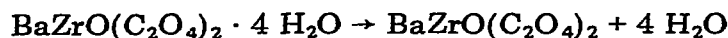
$BaZrO(C_2O_4)_2 \cdot 4\ H_2O \rightarrow BaZrO(C_2O_4)_2 + 4\ H_2O$

Step II: initial oxalate decomposition

$2\ BaZrO(C_2O_4)_2 \rightarrow Ba_2Zr_2O_2(C_2O_4)_3CO_3 + CO$

Step III: final oxalate decomposition

$Ba_2Zr_2O_2(C_2O_4)_3CO_3 \rightarrow Ba_2Zr_2O_5CO_3(CO_2) + 2\ CO_2 + 3\ CO$
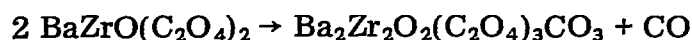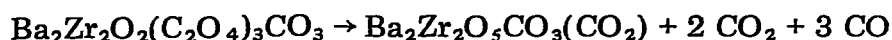
Step IV: evolution of entrapped CO_2

$$Ba_2Zr_2O_5CO_3(CO_2) \rightarrow Ba_2Zr_2O_5CO_3 + CO_2$$

Step V: decomposition of carbonate

$$Ba_2Zr_2O_5CO_3 \rightarrow 2\ BaZrO_3 + CO_2$$
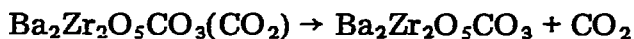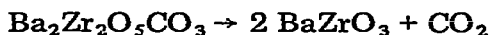
Scheme III

Step I: dehydration

$$PbZrO(C_2O_4)_2 \cdot 4\ H_2O \rightarrow PbZrO(C_2O_4)_2 + 4\ H_2O$$

Step II: decomposition of oxalate

$$2\ PbZrO(C_2O_4)_2 \rightarrow Pb_2Zr_2O_5CO_3 + 4\ CO + 3\ CO_2$$

Step III: decomposition of carbonate

$$Pb_2Zr_2O_5CO_3 \rightarrow 2\ PbZrO_3 + CO_2$$
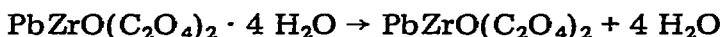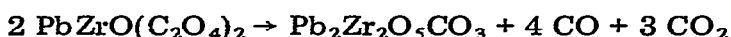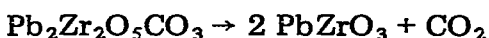
Calculation of the apparent activation energy, and order of reaction have been performed for the second and the last thermal decomposition reactions in nitrogen atmosphere employing the graphical method of Coats and Redfern [16]. The plot of $\{-\log\ [-\log\ (1-\alpha)/T^2]\}$ vs. $1/T \times 10^3$ for $n = 1$ (where n = apparent order of reaction) gives a straight line (Fig. 5) with slope $-E/2.303\ R$. Calculation of the heat of reaction from the DSC curves has been done using simple expression

$$\Delta H = KA/m$$

where ΔH is the heat of reaction, K is the calibration constant, A is the area under the peak, and m is the mass of the reactive compound.
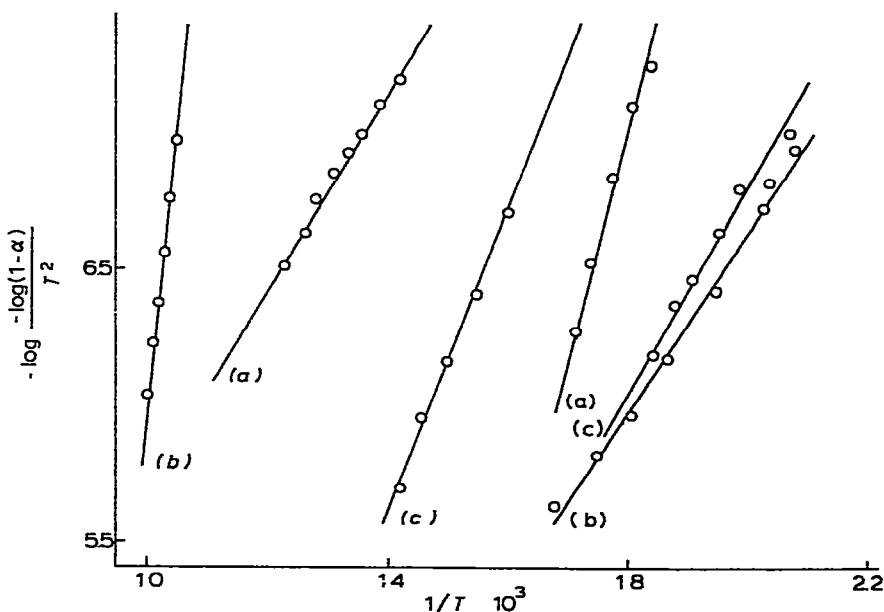

Fig. 5. Coats and Redfern linearization curves for the second (a, b, c) and last (a', b', c') steps of the decomposition reaction of MZO, BZO and LZO, respectively.

TABLE 1

Temperature range, weight loss, activation energy and heat of reaction for different decomposition steps of MZO, BZO and LZO

Decomposition step	Temp. range (K) in N_2 (in O_2)	% wt. loss		Heat of reaction (kcal mole^{-1})	Activation energy (kcal mole^{-1})	Order of reaction
		Calcd.	Obsd. in N_2 (in O_2)			
Decomposition of MgZrO $(C_2O_4)_2 \cdot 7 H_2O$						
1. Dehydration	298— 523 (303— 503)	29.06	29.01 (29.12)	26.35	38.76	1st
2. Initial oxalate decomposition	523— 593 (513—588)	19.84	19.72 (19.50)	27.44		
3. Final oxalate decomposition	593— 653 (588— 643)	8.30	8.45 (8.14)	43.29		
4. Decomposition of carbonate	673— 733 (673— 748)	5.07	5.07 (5.00)	7.57	15.5	1st
Decomposition of BaZrO$(C_2O_4)_2 \cdot 4 H_2O$						
1. Dehydration	333— 473 (333— 473)	14.62	14.73 (14.80)	10.01		
2. Initial oxalate decomposition	473— 623 (473— 613)	2.84	2.78 (3.00)	48.94	13.73	1st
3. Final oxalate decomposition	623— 683 (613— 683)	17.46	17.50 (17.50)	7.81		
4. Evolution of entrapped CO_2	693— 933 (688— 933)	4.45	4.17 (4.60)			
5. Decomposition of carbonate	948—1013 (943—1023)	4.45	4.44 (4.40)		79.8	1st
Decomposition of PbZrO$(C_2O_4)_2 \cdot 4 H_2O$						
1. Dehydration	303— 453 (303— 463)	12.79	12.6 (13.07)	6.68		
2. Decomposition of oxalate	453— 593 (473— 583)	21.76	21.92 (21.54)	10.24	15.05	1st
3. Decomposition of carbonate	603— 723 (598— 743)	3.90	4.00 (3.85)	5.22	27.34	1st

The thermal stability data, mass loss, apparent activation energy and heat of reaction for different decomposition steps are given in Table 1.

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