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A COMPARATIVE STUDY OF THE THERMAL DECOMPOSITION KINETICS OF ZIRCONYL OXALATES OF CALCIUM AND STRONTIUM

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ABSTRACT

The thermal decomposition kinetics of calcium and strontium zirconyl oxalates have been studied in air using TG, DTG and DTA techniques under non-isothermal conditions. The reaction order, activation energy, pre-exponential factor and entropy of activation were computed by means of the Freeman–Carroll, Coats–Redfern and Horowitz–Metzger equations, using the least squares method, for each step of decomposition. The values of A, $E^{\star}$ and $\Delta S^{\star}$ obtained by the three methods agree well.

INTRODUCTION

The zirconates and titanates of bivalent metals are of technological importance because of their electrical, magnetic and optical properties. Zirconyl oxalates of alkaline earth metals and lead have been found to offer a low-temperature route for the synthesis of pure and stoichiometric metazirconates. Several authors [1–4] have reported on methods of preparation for and the thermal behaviour of zirconyl oxalates of some bivalent metals. However, the literature on their thermal decomposition kinetics is rather scanty. As part of our investigations of the thermal behaviour of zirconyl oxalates of bivalent metals [5,6], we report here on the thermogravimetric analysis and kinetics of the thermal decomposition of calcium and strontium zirconyl oxalates.

EXPERIMENTAL

Materials

AnalaR or 'pro analysi' grade reagents were used throughout. Calcium zirconyl oxalate heptahydrate (CZO) and strontium zirconyl oxalate tetrahy-

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drate (SZO) were prepared according to a previously reported procedure [4]. The compounds, of general formula $MZrO(C_2O_4)_2xH_2O$ (where M = Ca and $x = 7$, or M = Sr and $x = 4$), were characterized by chemical analyses [4].

Thermogravimetric analyses

The thermogravimetric measurements were carried out on a manual thermobalance which employed a sensitive quartz spring. The experimental set-up was similar to that of Hooley [7]. A sample mass of about 150 mg was placed in a platinum crucible; heating rate was 5 K min^{-1}. DTA in air was carried out in a unit similar to that reported earlier [8], with a heating rate of 12 K min^{-1} and a sample mass of 400 mg. Analytical procedures for the identification of residues and gaseous products of decomposition were the same as those reported earlier [9].

Computation

The computation for the evaluation of the kinetic parameters was performed using a program written in BASIC for a microcomputer (HCL system 4 1S, with 512K RAM).

RESULTS

Thermogravimetric (TG) traces

The TG traces for CZO and SZO are given in Figs. 1 and 2, together with the DTG and DTA traces. The TG traces were redrawn as plots of fraction decomposed α vs. temperature T, to yield the primary α–T values. The TG traces indicate that CZO and SZO undergo thermal decomposition in three stages.

Thermal behaviour

Table 1 summarizes the general thermal behaviour of CZO and SZO, including stability ranges, peak temperatures and mass loss data. There are three major decomposition steps: dehydration of the hydrate, decomposition of the oxalate to a carbonate, and finally decomposition of the carbonate to the corresponding metazirconate.

CZO becomes completely dehydrated in the temperature range 300–475 K, in two well resolved reversible steps (Fig. 1). First a tetrahydrate and then an anhydrous oxalate is formed. SZO also becomes dehydrated in two

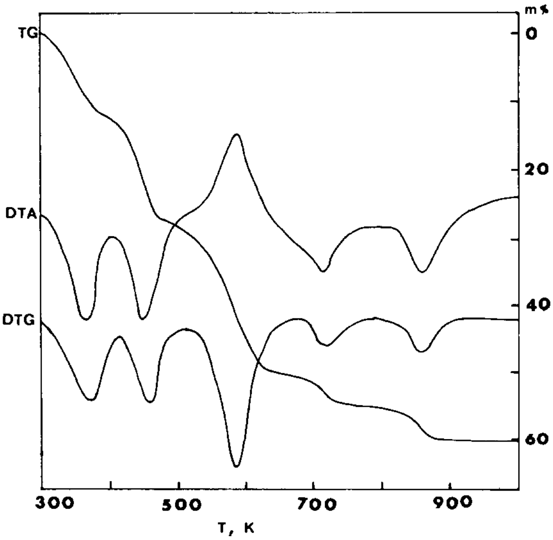

Fig. 1. TG, DTG and DTA traces for CZO.

well resolved steps (Fig. 2). First a dihydrate and later an anhydrous oxalate is formed.

The oxalate decomposition of CZO occurs in a single step in the temperature range 475–650 K, producing the carbonate. The observed mass loss of 22.4% is in good agreement with the theoretical value. The residue at this stage has the composition $Ca_2Zr_2O_4(CO_3)_2$, and is noncrystalline. The

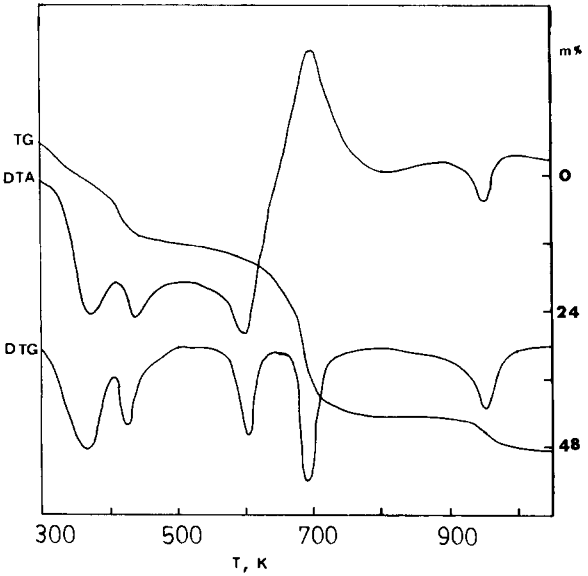

Fig. 2. TG, DTG and DTA traces for SZO.

TABLE 1

Thermal decomposition data

Compound	Decomposition step	Temperature range (K)	Peak temperature DTG (K)	Peak temperature DTA (K)	Loss of mass% Observed	Loss of mass% Theoretical
CZO	Oxalate decomposition	475–650	588	590	22.40	22.25
	First stage of carbonate decomposition	650–750	716	715	4.50	4.91
	Second stage of carbonate decomposition	800–880	858	860	5.37	4.89
SZO	First stage of oxalate decomposition	500–650	606	605	3.05	3.15
	Second stage of oxalate decomposition	650–750	689	690	22.50	24.39
	Decomposition of the carbonate	900–990	956	954	6.90	4.97

oxalate decomposition of SZO takes place in two steps. The first endothermic decomposition occurs in the temperature range 500–650 K, with a mass loss of 3.05%. The residue at this stage appears to have the composition $Sr_2Zr_2O_2(C_2O_4)_3CO_3$ [4]. The second stage of oxalate decomposition occurs in the temperature range 650–750 K, with a mass loss of 22.5%. This stage is exothermic because of the highly exothermic oxidation of carbon monoxide. The residue at this stage is found to have the composition $Sr_2Zr_2O_5CO_3$.

The carbonate $Ca_2Zr_2O_4(CO_3)_2$ decomposes in two steps. In the temperature range 650–750 K it decomposes to give $Ca_2Zr_2O_5CO_3$. The second step of carbonate decomposition occurs in the temperature range 800–880 K, giving $CaZrO_3$. The carbonate $Sr_2Zr_2O_5CO_3$ decomposes in a single step in the temperature range 900–990 K, giving $SrZrO_3$. In the case of both CZO and SZO, the final carbonate decomposition is accompanied by a simultaneous growth in particle size of the product.

Usually, in TG studies, more importance is given to the temperature range (i.e. the initial and final temperatures) than to the peak temperature, as the latter is dependent on variables such as sample size, surface area, heating rate, etc. [10,11]. On this basis, it may be concluded that SZO is thermally more stable than CZO.

Thermal decomposition kinetics

The thermal decomposition reactions of these compounds were studied using non-isothermal kinetic methods. The order of reaction n, and kinetic parameters such as the apparent activation energy $E^\star$, the entropy of activation $\Delta S^\star$, and the pre-exponential factor A were evaluated using the equations of Freeman–Carroll, Coats–Redfern and Horowitz–Metzger, employing the least squares method (LSM). In all cases the least squares plots were made by discarding the first few points (up to $\alpha = 0.15$) since these did not fall on the line. This was to be expected, since several authors [12,13] have reported that the decomposition of solids does not always obey first order kinetics in the initial stages. The procedures for the evaluation of the kinetic parameters are described briefly below.

Determination of the order of reaction

The order of each step of the decomposition reactions was determined by three different methods. The Freeman–Carroll equation [14] was used in the form

$$\frac{\Delta \ln (\mathrm{d}W/\mathrm{d}t)}{\Delta \ln W_\mathrm{r}} = \frac{-E^\star/R(\Delta T^{-1})}{\Delta \ln W_\mathrm{r}} + n \tag{1}$$

where $W_\mathrm{r} = W_\mathrm{c} - W$, W_c is the mass loss at the completion of the reaction, W is the total loss in mass up to time t, $\mathrm{d}W/\mathrm{d}t = (\mathrm{d}W/\mathrm{d}T)q$, R is the gas constant, and q represents the heating rate. The mass–temperature gradient $(\mathrm{d}W/\mathrm{d}T)$ can be obtained from TG data by employing Stirling's central difference formula [15]. The order was found by computing the intercept value of the least squares plot of $[\Delta(T^{-1})]/\Delta \ln W_\mathrm{r}$ vs. $[\Delta \ln(\mathrm{d}W/\mathrm{d}t)]/\Delta \ln W_\mathrm{r}$, and was found to be almost unity in all cases. Horowitz and Metzger [16] related n and the concentration of substance C_s present at the maximum rate of decomposition (i.e. at T_s, the DTG peak temperature) in the following way

$$C_\mathrm{s} = n^{(1/1-n)} \tag{2}$$

The order was determined using this relation according to the procedure described previously [6]. We also computed values of the correlation coefficient r using the LSM for the equations suggested by Coats and Redfern [17] (with $n = 0$, $1/2$, $2/3$ and 1), and obtained a maximum value for the equation with $n = 1$.

Evaluation of kinetic parameters

Using the above value of n, the kinetic parameters were evaluated using each of the following three non-mechanistic equations.

Freeman–Carroll:

$$\ln\left[\frac{\mathrm{d}W/\mathrm{d}t}{W_\mathrm{r}}\right] = \frac{-E^\star}{RT} + \ln A \tag{3}$$

Coats–Redfern:

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \frac{-E^\star}{RT} + \ln \frac{AR}{qE^\star} \tag{4}$$

TABLE 2

Kinetic data

Equation	Parameters [a]	CZO			SZO		
		Oxalate decomposition	First stage of carbonate decomposition	Final stage of carbonate decomposition	First stage of oxalate decomposition	Second stage of oxalate decomposition	Decomposition of the carbonate
Freeman–Carroll	$E^\star$	77.54	200.18	334.47	70.65	285.94	426.43
	A	1.02×10^{6}	9.88×10^{13}	1.21×10^{20}	2.13×10^{5}	1.48×10^{21}	9.78×10^{22}
	$\Delta S^\star$	−135.53	15.72	130.77	−148.81	153.40	185.53
	r	0.9998	0.9994	0.9995	0.9999	0.9997	0.9993
Coats–Redfern	$E^\star$	72.43	190.01	321.97	60.81	278.78	409.09
	A	3.35×10^{5}	1.62×10^{13}	1.04×10^{19}	1.73×10^{4}	4.77×10^{20}	5.88×10^{21}
	$\Delta S^\star$	−144.78	0.704	110.34	−169.70	143.99	162.16
	r	0.9999	0.9999	0.9999	0.9998	0.9987	0.9994
Horowitz–Metzger	$E^\star$	84.90	205.76	340.55	73.75	294.16	429.77
	A	5.14×10^{6}	2.48×10^{14}	1.50×10^{20}	2.74×10^{5}	7.45×10^{21}	2.73×10^{23}
	$\Delta S^\star$	−122.08	23.37	132.57	−146.69	166.85	194.07
	r	0.9990	0.9996	0.9997	0.9988	0.9991	0.9996

[a] Units: $E^\star$, kJ mol^{-1}; A, s^{-1}; $\Delta S^\star$, J K^{-1} mol^{-1}.

Horowitz–Metzger:

$$\ln[-\ln(1-\alpha)] = \frac{E^\star\theta}{RT_s^2} \tag{5}$$

where $\theta = T - T_s$.

In the case of eqns. (3) and (4) the LHS was plotted against reciprocal absolute temperature, and $E^\star$ and A were calculated from the slope and intercept, respectively. In the case of eqn. (5) a least squares plot was made of $\ln[-\ln(1-\alpha)]$ vs. θ, and $E^\star$ was calculated from the slope. The value of A was calculated using the equation

$$\frac{E^\star}{RT_s^2} = \frac{A}{q\,\exp(E^\star/RT_s)} \tag{6}$$

The entropy of activation was calculated using the relation

$$A = \frac{kT_s}{h}\exp(\Delta S^\star/R) \tag{7}$$

where k is the Boltzmann constant and h is the Planck constant.

DISCUSSION

The analyses of data using the Freeman–Carroll, Coats–Redfern and Horowitz–Metzger equations showed that the order of reaction for all stages of the decomposition of CZO and SZO is unity. The kinetic parameters were evaluated accordingly, for all the decomposition steps of these compounds, by the methods described above. The resulting values are presented in Table 2, together with the values of r for the corresponding least-squares plots. The satisfactory values of r in all cases ($r \approx 1$) indicate good agreement with the experimental data. The values of the kinetic parameters obtained using the Freeman–Carroll, Coats–Redfern and Horowitz–Metzger methods are comparable and in good agreement.

CZO and SZO have different decomposition patterns. The oxalate decomposition of CZO and the first stage of the oxalate decomposition of SZO are very slow and have negative values of $\Delta S^\star$, indicating that the activated complexes at these stages have a more ordered structure than the reactants, and that the reactions are slower than normal [18]. The last two stages of decomposition of the compounds are faster, and have positive values for the entropy of activation.

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