

Thermal decomposition kinetics of zirconyl oxalate, zirconyl oxalic acid and ammonium zirconyl oxalate

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Abstract

The thermal decomposition studies of zirconyl oxalate (ZO), Zirconyl oxalic acid (HZO) and ammonium zirconyl oxalate (NZO) have been carried out in air by TG, DTG and DTA techniques. The kinetic parameters (non-isothermal method) for their main oxalate decomposition step have been evaluated using the method suggested by Horowitz and Metzger. The results indicate that the values of E and A for the main oxalate decomposition step of these compounds are in the order $ZO \approx HZO < NZO$.

INTRODUCTION

The zirconates of bivalent metals are of technological importance because of their electrical and magnetic properties. These properties are greatly influenced by the method of preparation. Chemical methods yield products of high purity and controlled particle size. Barium zirconyl oxalate has been found to be the ideal precursor for the preparation of stoichiometric barium zirconate. The acid and ammonium zirconyl oxalates are found to be ideal starting materials for the preparation of stoichiometric barium zirconyl oxalate.

Several authors [1–3] have reported the thermal behaviour of zirconyl oxalates of barium and calcium. However, thermal decomposition studies on complex oxalates like zirconyl oxalic acid, ammonium zirconyl oxalate etc. are scarce. In an earlier paper [4] we reported on the thermal behaviour of zirconyl oxalate, zirconyl oxalic acid and ammonium zirconyl oxalate and proposed possible schemes for their decomposition. However, complete and reliable data on the thermal decomposition kinetics of these compounds are not available. In this paper we describe the thermogravimetric analysis and kinetics of the main oxalate decomposition step of zirconyl oxalate, zirconyl oxalic acid and ammonium zirconyl oxalate.

EXPERIMENTAL

Materials

All the reagents used were either BDH (AnalaR) or E. Merck (pro analysi) grade. Several methods [5,6] have been reported for the preparation of zirconyl oxalate. In the present investigation, $\text{ZrOC}_2\text{O}_4 \cdot 5.5\text{H}_2\text{O}$ (ZO) was prepared as follows. A solution of oxalic acid (1.174 g) in water (35 ml) was added dropwise to a solution of zirconyl oxychloride (3 g) in distilled water (50 ml). The solid compound that precipitated was filtered off, washed several times with water and finally with acetone and air dried. The results of wet-chemical analysis of the air dried compound gave the formula $\text{ZrOC}_2\text{O}_4 \cdot 5.5\text{H}_2\text{O}$. Zirconyl oxalic acid trihydrate, $\text{H}_2\text{ZrO}(\text{C}_2\text{O}_4)_2 \cdot 3\text{H}_2\text{O}$ (HZO), was prepared by a reported procedure [7]. The ammonium salt, $(\text{NH}_4)_2\text{ZrO}(\text{C}_2\text{O}_4)_2 \cdot 3\text{H}_2\text{O}$ (NZO), was obtained by passing through the freshly prepared acid dry ammonia diluted with nitrogen.

Methods

The thermogravimetric measurements were carried out on a manual thermobalance which incorporated a sensitive quartz spring. The experimental set-up was similar to that of Hooley [8]. A sample mass of about 150 mg was placed in a platinum crucible, and the heating rate was 5 K min^{-1} . DTA in air was carried out in a unit similar to that described earlier [9], 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 [10].

The numerical analysis of the thermogravimetric data was realized using a program written in MICROSOFT BASIC for an IBM computer using DOS 4.00.

THEORETICAL

In recent years, there has been increasing interest in determining the rate dependent parameters of solid-state non-isothermal decomposition reactions from an analysis of the thermogravimetric curve. Several authors [11–18] have discussed the advantages of this method over the conventional isothermal method. The rate of reaction of a substrate under non-isothermal conditions is generally expressed by the relation [11]

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where α represents the fraction of the reactant transformed at time t , $f(\alpha)$ is the conversion function of α dependent on the mechanism of the reaction, and $k(T)$ is the rate constant, and dependent on the temperature. In the

study of chemical reactions, the temperature dependent function $k(T)$ is of the Arrhenius type [19,20] and can be considered as the rate constant k

$$k = A e^{-E/RT} \quad (2)$$

where A is the pre-exponential factor, E is the activation energy and R is the gas constant.

Combining eqns. (1) and (2) we obtain

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{q} e^{-E/RT} dT \quad (3)$$

where q is the linear heating rate, dT/dt . Equation (3), on integration and taking logarithms, yields

$$\ln g(\alpha) = \ln[AE/qR] + \ln p(x) \quad (4)$$

where

$$p(x) = \int_x^\infty \frac{e^{-x}}{x^2} dx \quad \text{and} \quad x = E/RT$$

This is the basic form of the equation used for analysing non-isothermal data. This equation can be readily applied once the form of the function $p(x)$ is established. Horowitz and Metzger [15] simplified the exponential integral by defining a characteristic temperature deviation, θ , such that $T = T_s + \theta$, where T_s is the DTG peak temperature. Using this definition for θ in eqn. (4), these authors derived the following equations

$$\ln[1 - (1 - \alpha)^{1-n}] = \frac{-E\theta}{RT_s^2} + \ln(1 - n) \quad (\text{for } n \neq 1) \quad (5)$$

and

$$\ln[-\ln(1 - \alpha)] = \frac{-E\theta}{RT_s^2} + C \quad (\text{for } n = 1) \quad (6)$$

where C is a constant.

The form of representation of the above equations seems to suggest the application of the least-squares method (LSM) to the relationship $y = mx + b$. The least-squares analysis is based on the observation that, often, random experimental errors closely follow a Gaussian distribution. This assumption fails when y contains a logarithmic function, because use of the logarithmic function tends to compress the high values while expanding the low values. This defect can be remedied by using the weighted LSM. Several authors [21–23] have reported that the best fit of their experimental and calculated data was obtained using the weighted LSM. The weights used most often are the inverses of the dependent variables [24]. It has been shown [21] that the deviation S_α^2 of the variable α is proportional to $1 + \alpha^2$. Multiplication of

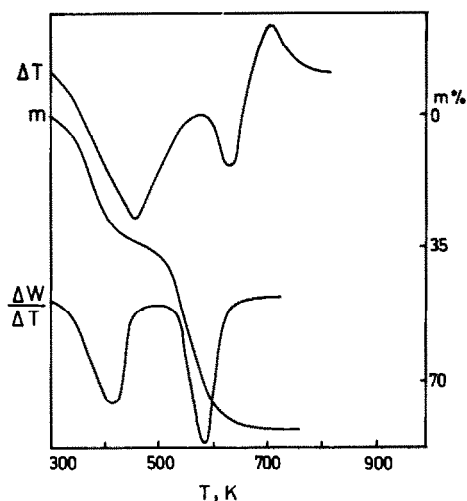


Fig. 1. TG, DTG and DTA traces of ZO.

the deviation by a constant value does not influence the results of calculation [21,25]. Thus, for calculation of weights one can use

$$S_{\alpha}^2 = 1 + \alpha^2 \quad (7)$$

Transforming α into y , one should also correspondingly transform S_{α}^2 into S_y^2 . The deviation of y is calculated from the transformed formula

$$S_y^2 = S_{\alpha}^2 \left[\frac{\partial y}{\partial \alpha} \right]^2 \quad (8)$$

and the following is used as the weight (w) for the weighted least-squares fit

$$w = 1/S_y^2 \quad (9)$$

RESULTS

The TG curves were studied in greater detail. The TG, DTG and DTA traces are given in Figs. 1–3. The main oxalate decomposition reactions of the above three compounds were subjected to non-isothermal kinetic studies. The order of the reaction (n) and kinetic parameters such as apparent activation energy (E), the entropy of activation (ΔS) and the pre-exponential factor (A) were evaluated.

Evaluation of kinetic parameters

The Freeman–Carroll equation [13] was used in order to determine the order of the reaction, but its applicability was found to be extremely poor, as observed from the scattered plot. Several authors [26–28] have made

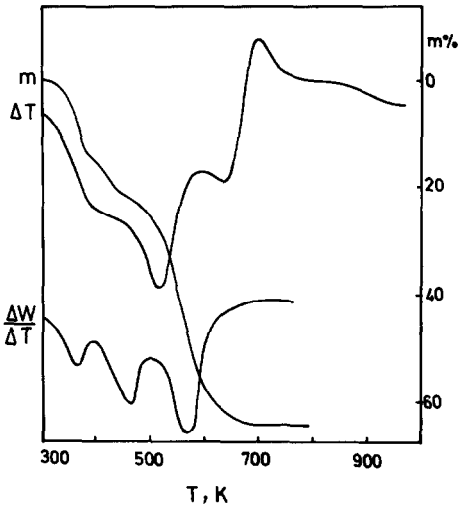


Fig. 2. TG, DTG and DTA traces of HZO.

similar observations. Therefore attempts have been made to apply the method suggested by Horowitz and Metzger [15]. They related the concentration of substance (C_s) present at the maximum rate of decomposition (i.e. at T_s , the DTG peak temperature) and the reaction order n in the following way

$$C_s = n^{(1/1-n)} \quad (10)$$

Determination of n directly from C_s is complicated, and hence a “master curve” between C_s and n was constructed as reported in earlier work [29].

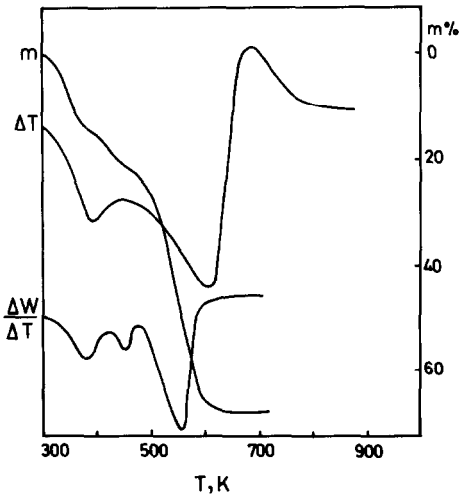


Fig. 3. TG, DTG and DTA traces of NZO.

The value of n corresponding to the experimentally determined value of C_s was read off from the master curve. It was found that the order of the main oxalate decomposition step of each of the three compounds was near unity. We also computed the values of the correlation coefficient for the equations suggested by Coats and Redfern [14] (with $n = 0, 1/2, 2/3$ and 1) and obtained the maximum value for the equation with $n = 1$.

Accordingly, the kinetic parameters for the main oxalate decomposition step were evaluated using the equation suggested by Horowitz and Metzger [15] for first order kinetics

$$\ln[-\ln(1-\alpha)] = \frac{-E\theta}{RT_s^2} \quad (11)$$

The weighted least-squares plot of $\ln[-\ln(1-\alpha)]$ against θ was found to be linear; E was calculated from the slope. A was calculated using the equation

$$\frac{E}{RT_s^2} = \frac{A}{q \exp(E/RT_s)} \quad (12)$$

and the entropy of activation (ΔS) was calculated using the following relation

$$A = \frac{kT_s}{h} \exp(\Delta S/R) \quad (13)$$

where k is the Boltzmann constant and h is the Planck constant. All the weighted least-squares plots for the Horowitz–Metzger equation were drawn discarding the first few points (up to $\alpha = 0.15$), since they did not fall on the line and hence their inclusion would have resulted in poor correlation (Fig.

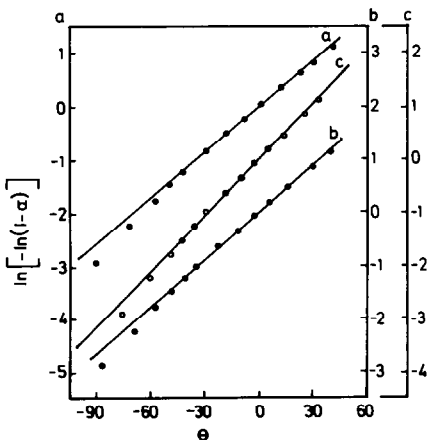


Fig. 4. Horowitz–Metzger plot for curve a = ZO, curve b = HZO and curve c = NZO.

TABLE 1

Thermal decomposition data

Compound	Nature of decomposition step	Temperature range (K)	Peak temperature in DTG (K)	Loss of mass (%)	
				Observed	Theoretical
ZO	Dehydration	300–465	400	25.10	24.47
	Oxalate decomposition	465–650	581	57.89	58.12
HZO	Dehydration	300–380	368	14.50	15.92
	Low temperature oxalate decomposition	380–460	450	8.10	6.19
	Main oxalate decomposition	460–640	573	41.68	41.57
NZO	Dehydration	300–400	380	13.50	14.47
	Low temperature oxalate decomposition	400–460	452	7.41	5.63
	Main oxalate decomposition	460–625	556	46.31	46.83

4). This is as expected, since the decomposition of solids is known not to obey first order kinetics in the initial stages [30,31].

DISCUSSION

The general thermal behaviour of the compounds, such as the temperature range of each step of decomposition, DTG peak temperatures, mass loss data, etc., is listed in Table 1. The values of kinetics parameters for the main oxalate decomposition step are given Table 2.

For ZO there are two major decomposition steps. In the first step four molecules of water are eliminated, as is shown by the DTG peak around 400 K. The corresponding mass loss, 25.1%, is in agreement with the calculated value of 24.47%. The remaining water molecules are eliminated in the temperature range 465–650 K; the corresponding peak is not resolved since

TABLE 2

Kinetic data for the main oxalate decomposition step

Compound	E (kJ mol ⁻¹)	A (s ⁻¹)	ΔS (J K mol ⁻¹)	r
ZO	80.09	2.26×10^6	-128.81	0.9999
HZO	80.96	3.56×10^6	-124.93	0.9998
NZO	88.63	3.66×10^7	-105.31	0.9999

it overlaps with the oxalate decomposition step. Thus, the oxalate decomposition takes place in an atmosphere of water vapour and hence the corresponding DTA peak appears as an endotherm. The main oxalate decomposition occurs between 465 and 650 K. The DTG peak around 581 K and the endothermic DTA peak around 628 K represent this stage. The observed mass loss for the oxalate decomposition is 57.89%, as against the expected 58.12%. The exothermic DTA peak seen around 715 K, unaccompanied by mass loss, is attributed to the crystallization of amorphous zirconium dioxide to the monoclinic form. The isothermal heating of ZO (for 3 days at 600 K) established that the residue is monoclinic zirconium dioxide.

HZO becomes completely dehydrated in a single step shown by the DTG peak around 368 K. The initial mass loss in TG agrees well with the theoretically expected loss due to the elimination of three molecules of water. The oxalate decomposition occurs in two steps. The first step of the oxalate decomposition overlaps with the dehydration step and appears as an endotherm around 513 K in DTA. The first step of oxalate decomposition produces an oxalato-carbonate intermediate of apparent composition $\text{H}_2\text{ZrO}(\text{C}_2\text{O}_4)_{2-x}(\text{CO}_3)_x$, where $0.5 < x < 1$. The main oxalate decomposition occurs between 460 and 640 K. The DTG peak at 573 K represent this stage. The final residue is found to be monoclinic zirconium dioxide.

The complete dehydration of NZO also takes place in a single step shown by the DTG peak around 380 K and the corresponding DTA peak around 388 K. The anhydrous compound can be isolated by isothermal heating of NZO at 375 K. The two steps of oxalate decomposition are quite distinct in DTG, whereas they overlap on the DTA curve. The first step of the oxalate decomposition results in an oxalato-carbonate intermediate, $(\text{NH}_4)_2\text{ZrO}(\text{C}_2\text{O}_4)_{2-x}(\text{CO}_3)_x$, with $0.5 < x < 1$. The DTG peak around 452 K represents this stage. The main oxalate decomposition takes place in the temperature range 460–625 K, and the corresponding DTG peak is observed around 556 K. The final residue is found to be monoclinic zirconium dioxide.

The analysis of data using the Horowitz–Metzger equation showed that the order of the main oxalate decomposition step of all the compounds is near to unity. Based on this value of reaction order, the kinetic parameters were evaluated using the above equation. It is observed that the values of E and A increase in the order $\text{ZO} \approx \text{HZO} < \text{NZO}$. This can be attributed to the difference in the reaction intermediates. The main oxalate decomposition of HZO starts from the intermediate $\text{H}_2\text{ZrO}(\text{C}_2\text{O}_4)_{2-x}(\text{CO}_3)_x$, while that of NZO starts from $(\text{NH}_4)_2\text{ZrO}(\text{C}_2\text{O}_4)_{2-x}(\text{CO}_3)_x$. Because of their similar structures [4], HZO and NZO show similar thermal behaviour, as evidenced by their peak temperatures and comparable values of E and A . The entropy of activation varies from -105.31 to $-128.81 \text{ J K mol}^{-1}$. The negative values indicate that the activated complexes have a more ordered structure than the reactants, and that the reactions are slower than normal [32].

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