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KINETICS OF THERMAL DECOMPOSITION OF SOME METAL OXALATES

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ABSTRACT

The thermal decomposition kinetics of oxalates of Zn^{II}, Ni^{II} and Th^{IV} have been studied in air by isothermal and non-isothermal thermogravimetry. The isothermal kinetic results suggest that the mechanism of decomposition of the zinc compound involves rapid nucleation followed by two dimensional growth in the acceleratory region, while in the case of thorium oxalate, the initial nucleation occurs by a chain mechanism on the surface of the reactant followed by the growth of the product from the surface towards the interior. The results on nickel oxalate could not be interpreted in an unambiguous manner. The activation energy and the frequency factor obtained from TG curves compare well with those obtained from the isothermal method. The activation energies for the dehydration of these oxalates have also been evaluated from the thermogravimetric curves.

INTRODUCTION

In recent years, there is a renewed interest in the study of kinetics and mechanism of solid state thermal dehydration and decomposition reactions of simple metal salts such as oxalates[1], acetates[2], perchlorates[3] and sulphates[4]. In general, the kinetics of solid state thermal decomposition can be followed either by isothermal or non-isothermal (dynamic) methods. The data obtained from the isothermal method are usually presented in terms of the fraction of the reactant decomposed (x) as a function of time (t). These sigmoid shaped curves are characteristic[5] of a mechanism by which the decomposition occurs at the interface between the product and the undecomposed reactant. The kinetic data are usually analysed through various kinetic expressions (Table I) derived in terms of nucleation and growth of the nuclei[5]. The kinetic parameters for the thermal decomposition of solids can also be obtained from thermogravimetric (TGA) curves. However, such an analysis is difficult as both temperature (T) and time (t) are simultaneously kept as variables during a TGA run. Nevertheless, approximate methods have been developed for the analysis of TGA curves by Freeman and Carrol[6], Coats and Redfern[7] and Zsako[8]. In this investigation, the kinetics of thermal decomposition of three simple oxalates, namely of Ni^{II}, Zn^{II} and Th^{IV} have been studied by isothermal and non-isothermal thermogravimetry, with a view to obtaining the kinetic parameters and to critically comparing the data obtained by both the methods.

TABLE I

KINETIC EQUATION FOR ISOTHERMAL DECOMPOSITIONS OF SOLIDS

Equation	*Function plotted*
Simple power law	$\log \alpha$ *vs.* $\log t$
Prout–Tompkins law	$\log \left(\frac{\alpha}{1-\alpha}\right)$ *vs.* t
Avrami–Erofeyev equation	$\log \left[\log \left(\frac{1}{1-\alpha}\right)\right]$ *vs.* $\log t$
Unimolecular law	$\log \left(\frac{1}{1-\alpha}\right)$ *vs.* t
Exponential law	$\log \alpha$ *vs.* t
Contracting cube law	$[1-(1-\alpha)^{1/3}]$ *vs.* t

EXPERIMENTAL

Nickel (II) oxalate dihydrate, zinc (II) oxalate dihydrate and thorium (IV) oxalate hexahydrate were prepared by standard methods. Their compositions were ascertained by the chemical analyses of the metal and oxalate contents.

Thermogravimetric analysis of the compounds in air was carried out with a Stanton thermobalance model HT-SM. The heating rate was 6°C·min^{-1}. A constant quantity of 200 mg of the hydrated sample was employed for each run. Isothermal decompositions were also carried out with the same thermobalance. The samples were first dehydrated *in situ* at the appropriate temperature and then cooled in a desiccator. In the meantime, the furnace temperature was raised to the required value and the sample then introduced into the furnace. The weight loss is recorded as a function of time at various constant temperatures. Typical isothermal decomposition curves obtained in the case of thorium oxalate are given in Fig. 1. These curves were analysed

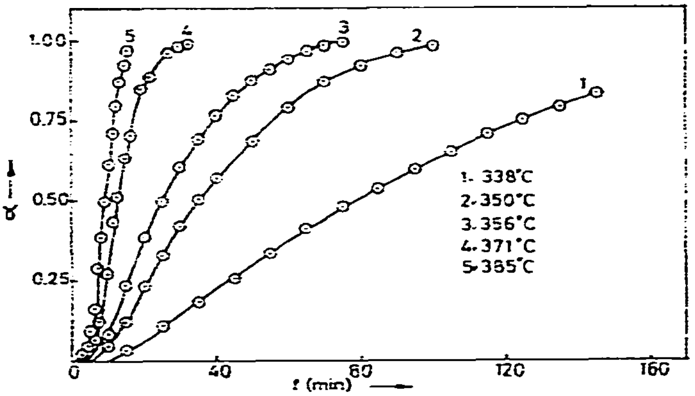

Fig. 1. Isothermal decomposition curves of $Th(C_2O_4)_2$.

through various kinetic equations by plotting suitable functions of α and t, given in Table I. A linear relationship (Figs. 2–8) is indicative of the applicability of any

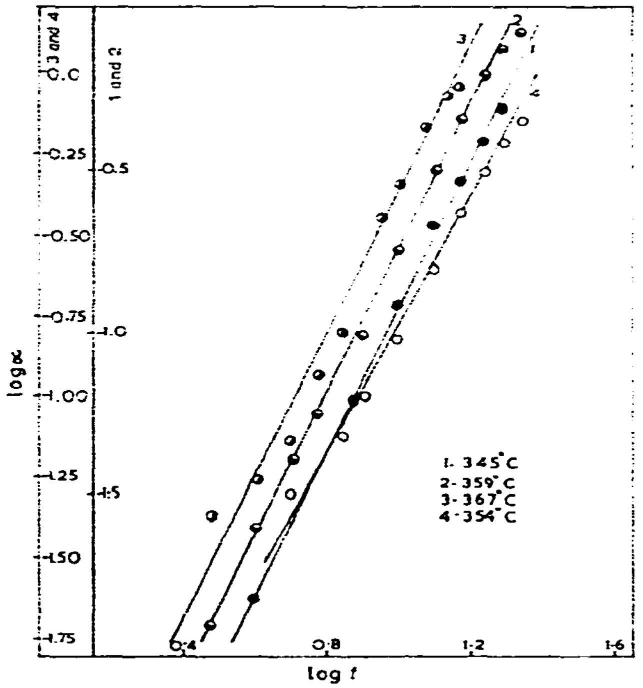

Fig. 2. Decomposition of zinc oxalate: Simple power law.

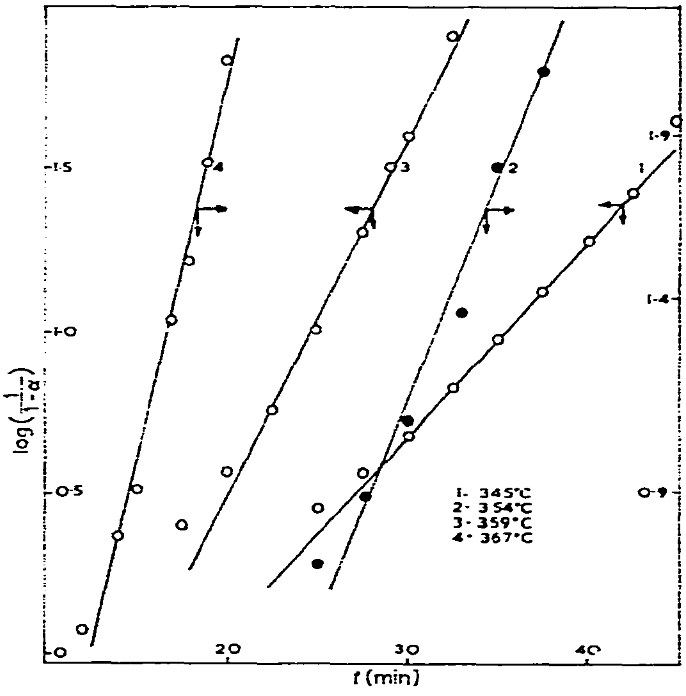

Fig. 3. Decomposition of zinc oxalate: Unimolecular law.

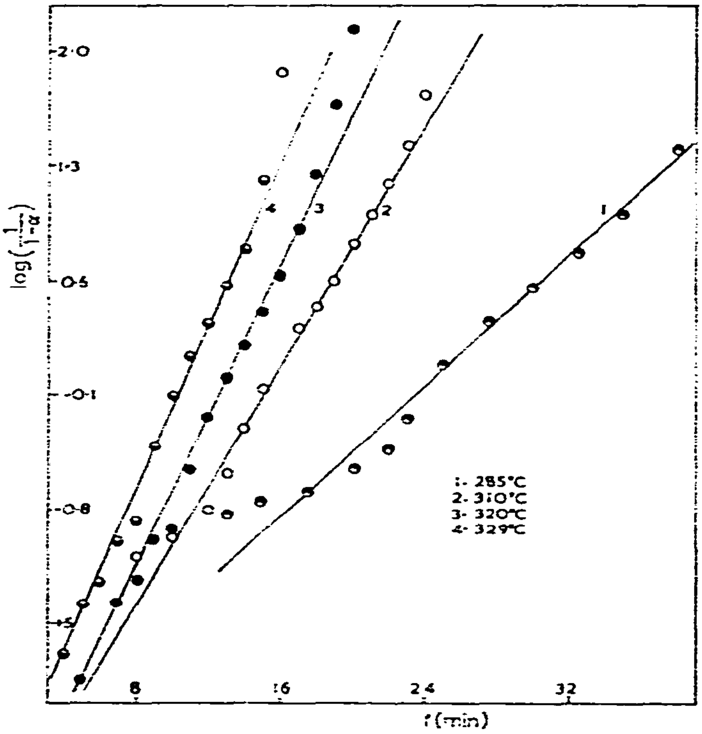

Fig. 4. Decomposition of nickel oxalate: Prout–Tompkins equation.

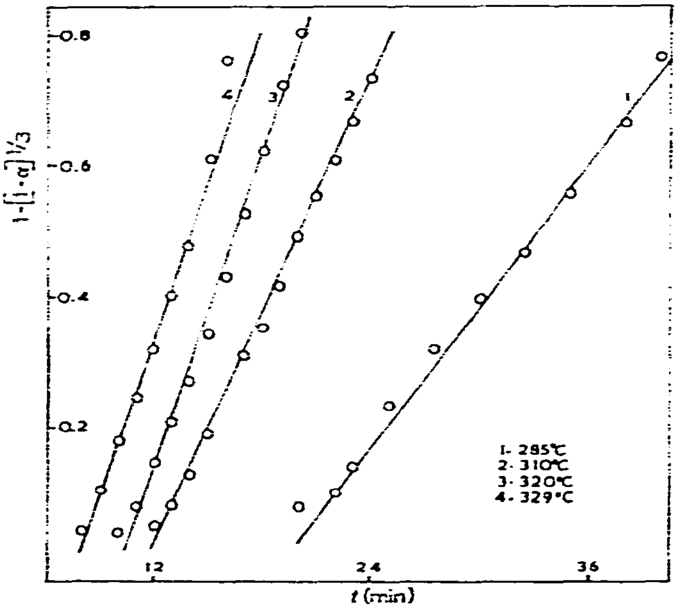

Fig. 5. Decomposition of nickel oxalate: Contracting cube law.

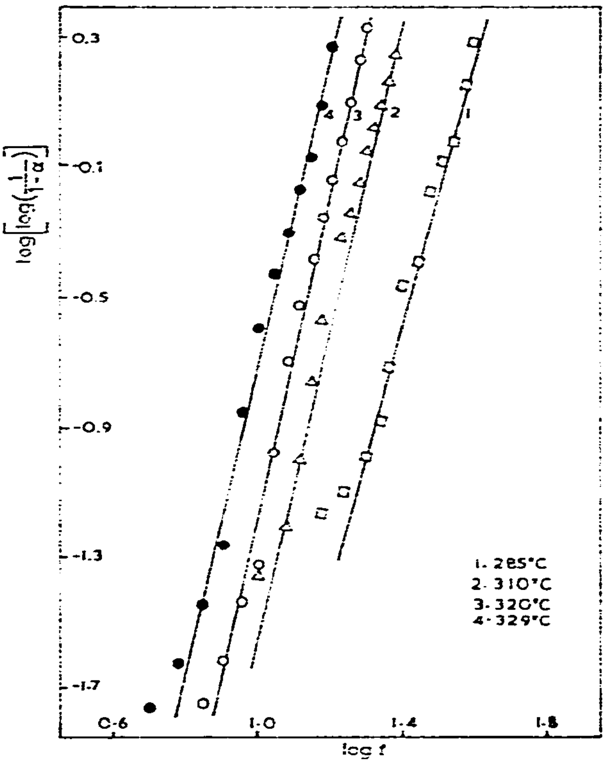

Fig. 6. Decomposition of nickel oxalate: Avrami equation.

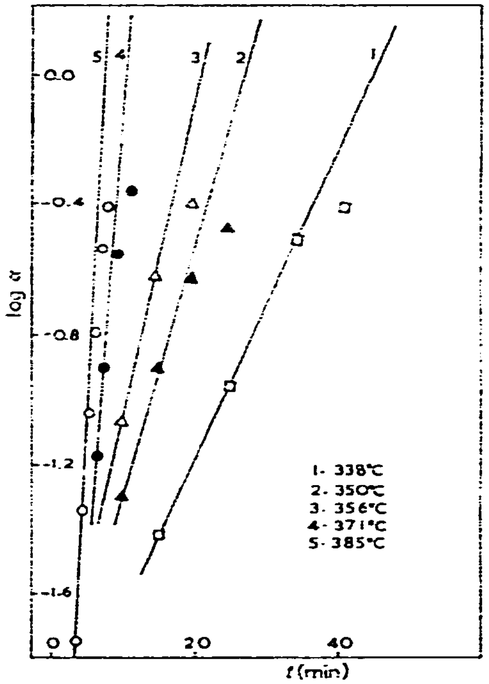

Fig. 7. Decomposition of thorium oxalate: Exponential law.

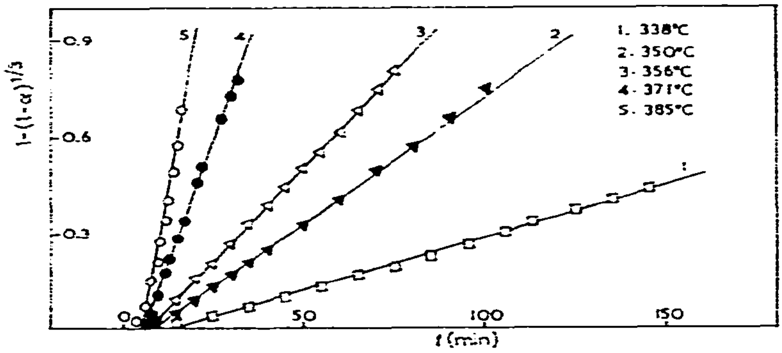

Fig. 8. Decomposition of thorium oxalate: Contracting cube law.

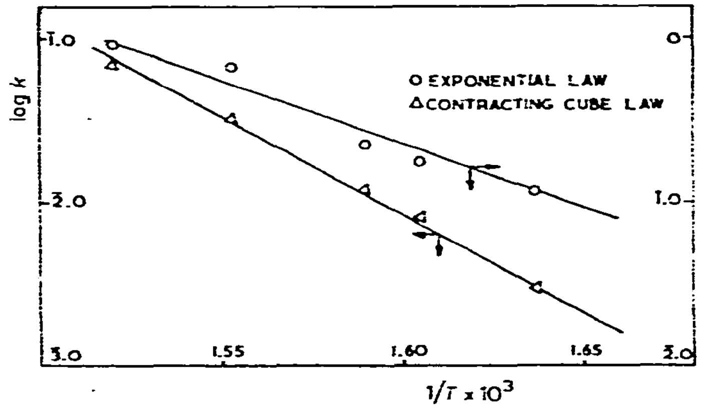

Fig. 9. Decomposition of $Th(C_2O_4)_2$: Arrhenius plot.

particular equation in the corresponding region of α. k values for the linear region were calculated from the appropriate equations. The activation energy E, and the frequency factor Z were evaluated from Arrhenius plots. The kinetic parameters were also calculated from the TG curves by the methods of Coats and Redfern[7] and of Zsako[8]. The results are presented in Table II.

RESULTS AND DISCUSSION

Zinc oxalate

The decomposition of zinc oxalate in air has been studied by Dollimore *et al*[9]. who have found that the power law is applicable during the acceleratory region with the value of n varying between 1.5 and 1.8 Yankwich *et al.*[10] during their studies on the decomposition of anhydrous zinc oxalate in vacuum have reported that the data obey a power law with $n = 1$ to 2 in the acceleratory region and unimolecular law towards the final stages of the reaction with activation energies of 53 ±5 and 51 ±2 kcal·mole^{-1}, respectively.

From our results the decomposition of zinc oxalate in air in the temperature range 340–370°C is found to obey the simple power law with $n = 2$ to 2.2 in the region

TABLE II

RESULTS OF THE DECOMPOSITION OF SOME METAL OXALATES

Method and name of the equation	*Validity range of* α	*Energy of activation E* ($kcal \cdot mole^{-1}$)	*Arrhenius parameter Z* (min^{-1})
(a) Zinc oxalate			
Isothermal method			
1 Simple power law	0.05–0.65	60.8	3.0×10^{18}
2 Unimolecular law	0.80–1.0	62.7	2.8×10^{21}
Dynamic method			
1 Coats and Redfern equation	—	62.2	4.8×10^{20}
2 Zsako's method	—	52.0	2.6×10^{17}
(b) Nickel oxalate			
Isothermal method			
1 Prout–Tompkins model	0.015–0.96	13.2	3.7×10^{4}
2 Contracting cube law	0.25–0.99	19.8	6.9×10^{7}
3 Avrami–Erofeyev law	0.08–0.98	16.0	8.0×10^{4}
4 Unimolecular law	0.80–1.0	33.2	1.8×10^{11}
Dynamic method			
1 Coats and Redfern equation	—	38.8	1.1×10^{13}
2 Zsako's method: Avrami equation with $n = 2$	—	34.0	2×10^{12}
(c) Thorium oxalate			
Isothermal method			
1 Exponential law	0–0.15	35.6	6.8×10^{11}
2 Contracting cube law	0.12–1.0	54.6	1.2×10^{17}
Dynamic method			
1 Coats and Redfern equation	—	50.7	9.4×10^{16}
2 Zsako's method			
a Contracting cube law	—	42.0	3×10^{13}
b Unimolecular law	—	42.0	1×10^{14}

$0.05 < \alpha < 0.65$ and a unimolecular law towards the final stages of the reaction ($0.8 < \alpha < 1.0$). A value of $n = 2$ in power law can be interpreted in two ways[5]: either it is due to random nucleation followed by one dimensional growth or it is due to extremely rapid nucleation followed by two dimensional growth. One dimensional growth of nuclei being a very slow method of propagating reaction in a three dimensional solid matrix, it is probable that in the present case the reaction occurs by extremely rapid random nucleation followed by two dimensional growth. Generally towards the end of the reaction, the reactant-product interface is of complex shape. Due to the strain created at this interface, it breaks into smaller chunks of reactant which do not contain any nuclei. So in these chunks, each molecule has got an equal chance of decomposition, thus obeying unimolecular law towards the final stages of the reaction. This is in good agreement with the results of Yankwich *et al.*[10]. The intermediate region ($0.65<\alpha<0.8$) could not be analysed satisfactorily by any single kinetic expression. This may be attributed to the fact that a combination of various kinetic laws may be operative in this region.

The activation energies for zinc oxalate decomposition from the TG curves by the methods of Coats and Redfern and Zsako are in satisfactory agreement with the value obtained by isothermal method (Table II).

Nickel oxalate

The thermal decomposition of nickel oxalate in vacuum[11] giving metallic nickel as the final product has been found to follow the Avrami–Erofeyev equation in the acceleratory region and the unimolecular law towards the end. The kinetics of decomposition of nickel oxalate in air has not been investigated previously. The final product of decomposition in air is nickel oxide.

In the present investigation, the decomposition of nickel oxalate has been carried out in air in the temperature range 280–330°C. The results can be fitted equally well into Prout–Tompkins law followed by contracting cube law or into Avrami–Erofeyev law in both the initial and acceleratory regions. This may mean that the reaction proceeds by either fast nucleation by branching chain mechanism on the surface followed by growth towards the interior or random nucleation followed by three dimensional growth, respectively. The results show the inadequacy of kinetic methods alone for the study of mechanisms of thermal decompositions of certain solids. However, the deceleratory region of the nickel oxalate decomposition ($0.8<\alpha<1.0$) is clearly governed by unimolecular law, as in the case of zinc oxalate.

Thorium oxalate

The kinetics of thermal decomposition of thorium oxalate have been studied previously only by non-isothermal methods[12,13] (DTA and TGA). In this investigation, the decomposition of the anhydrous compound in air has been studied in the temperature range 335–385°C. The reaction obeys an exponential law up to $\alpha = 0.1$ followed by contracting cube law till the end. The corresponding activation energies are 36 and 55 kcal·mole^{-1}. The applicability of these two kinetic expressions suggest that the nucleation occurs on the surface and grows fast by a chain mechanism in the early stages and soon a product layer covers the surface of the reactant. Further reaction proceeds by the growth of this product layer towards the interior. The gross activation energies obtained by Coats and Redfern and Zsako's methods from the TG curves are 51 and 42 kcal·mole^{-1}, respectively and these are in fair agreement with the average value obtained by the isothermal method. It may be noted here that while the methods available at present for the evaluation of kinetics from TG curves give satisfactory values of activation energy and frequency factor, they do not throw sufficient light on the mechanism of decomposition.

Kinetics of dehydration of hydrated oxalates from TG curves

The kinetic parameters for the dehydration of the oxalates have been calculated from the TG curves by Coats and Redfern[7] method. The activation energies are presented in Table III. The *E* values for the dehydration of oxalates and other similar compounds[14,15] are generally around 17–22 kcal·mole^{-1} as it is observed in the present work. This suggests that the nature of bonding of water molecules in the metal oxalates studied is similar. In the case of thorium oxalate, the dehydration occurs in two stages, the last water molecule being removed at a higher temperature with an activation energy of 30 kcal·mole^{-1}. This may be due to the structurally different mode of attachment of one water molecule in the compound.

TABLE III

DEHYDRATION OF SOME METAL OXALATES

Reaction	*E (kcal·mole^{-1})*	*Temperature range (°C)*
$ZnC_2O_4 \cdot 2H_2O \rightarrow ZnC_2O_4 + 2H_2O$	17.0	150–220
$NiC_2O_4 \cdot 2H_2O \rightarrow NiC_2O_4 + 2H_2O$	19.0	130–270
$Th(C_2O_4)_2 \cdot 6H_2O \rightarrow Th(C_2O_4)_2 \cdot H_2O + 5H_2O$	16.9	60–160
$Th(C_2O_4)_2 \cdot H_2O \rightarrow Th[C_2O_4]_2 + H_2O$	29.7	180–230

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