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Effect of γ-Radiation on the Thermal Decomposition of Zinc Oxalate

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The thermal decomposition of γ-irradiated zinc oxalate was studied by dynamic thermogravimetry. Kinetic parameters were calculated and compared with those of unirradiated sample. The E, Z and ΔS^* values showed a decrease. The effect of γ-irradiation on the mechanism of decomposition was also studied.

INTRODUCTION

The absorption of ionising radiations by substances results in a variety of physical and chemical consequences which depend on the nature of the system and the energy of incident radiation[1]. Irradiation may create many new potential nucleation centres which favour heterogeneous processes. In some cases the action of irradiation on the material may be electronic, while in others it may be structural.

Numerous irradiation effects on simple metal oxalates have been described[2–4]. In isothermal studies it has been observed that the rate constants for acceleratory and decay stages are enhanced[5–7]. Some other studies also stressed the importance of formation and growth of nucleation centres due to chemical and lattice defects created by irradiation[8–10].

EXPERIMENTAL

Zinc oxalate dihydrate with particle size in the range 90–106 microns was irradiated with Co-60 γ-radiation at room temperature. The sample was taken in glass ampoules and four doses *viz.*, 50 Mrad, 100 Mrad, 150 Mrad, and 200 Mrad were given to four samples. Dose rate was 0.07 Mrad per hour. The non-isothermal TG of four samples along with one unirradiated sample were taken in static air atmosphere with a heating rate of 5°C per minute, using shimadzu thermal analyser.

RESULTS AND DISCUSSION

$ZnC_2O_4 \cdot 2H_2O$ decomposed in two stages on heating:

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$$ZnC_2O_4 \cdot 2H_2O \rightarrow ZnC_2O_4 + 2H_2O \quad (1)$$

$$ZnC_2O_4 \rightarrow ZnO + CO + CO_2 \quad (2)$$

The effect of γ-irradiation on the second stage of decomposition is studied here. Kinetic parameters such as energy of activation E, frequency factor and entropy of activation ΔS^* were also calculated using Coats-Redfern (CR), Horowitz-Metzger (HM) and Freeman-Caroll (FC) methods[11–13]. These are given in Table-1.

In the present study, when compared to unirradiated samples the procedural temperature of decomposition T_i and final temperature of decomposition T_f showed an increase. Temperature of maximum decomposition T_S also showed an increase except in the case of the sample which was subjected to a dose of 100 Mrad. The activation energy E, frequency factor Z and entropy of activation ΔS^* showed, generally, a decrease. E and ΔS^* values recorded a minimum for 100 Mrad. (Fig. 1).

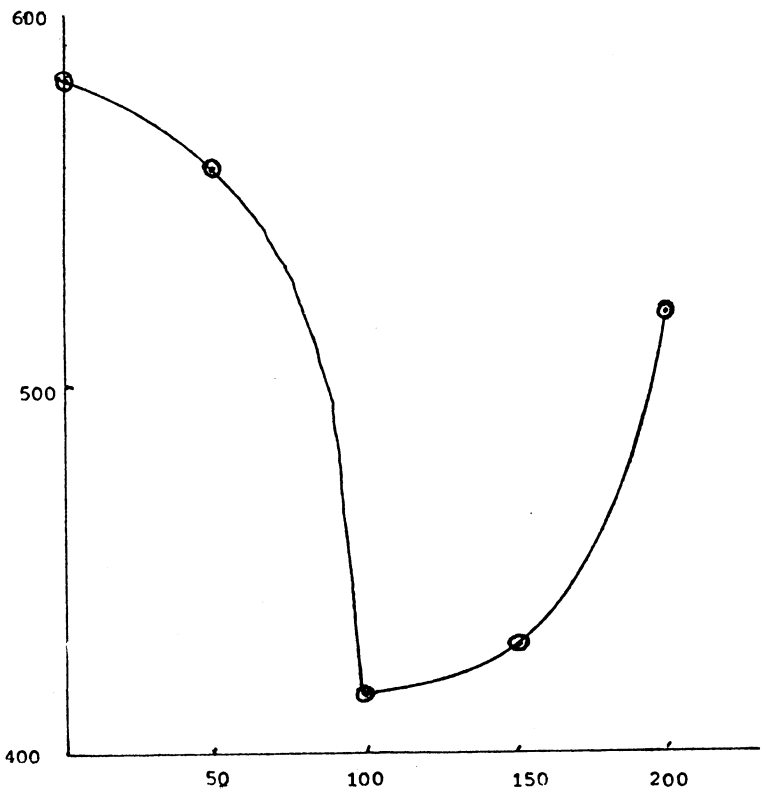

Fig. 1. Effect of γ-radiation on energy of activation

TABLE-1
EFFECT OF γ-IRRADIATION ZnC_2O_4

Static air atmosphere; Heating rate: 5 K min^{-1}; Mass of the sample in each case: 15 mg

Dose	T_j K	T_f K	T_s K	E (KJ per mol) CR	E (KJ per mol) HM	E (KJ per mol) FC	Z (min^{-1}) CR	Z (min^{-1}) HM	Z (min^{-1}) FC	ΔS^* (Jk^{-1} mol^{-1}) CR	ΔS^* (Jk^{-1} mol^{-1}) HM	ΔS^* (Jk^{-1} mol^{-1}) FC
Unirradiated	620.5	673.0	662.7	529.0	582.4	584.3	2.3×10^{45}	6.5×10^{41}	1.2×10^{46}	560.4	591.5	596.4
50 Mrad	641.5	692.0	680.2	534.5	560.3	585.9	3.1×10^{40}	7.7×10^{42}	6.7×10^{44}	489.6	535.3	572.7
100 Mrad	623.0	670.5	658.3	396.2	416.4	372.1	7.7×10^{30}	6.4×10^{32}	1.6×10^{29}	305.7	342.5	273.7
150 Mrad	638.0	686.0	667.0	419.2	429.6	333.5	1.1×10^{32}	2.5×10^{33}	2.6×10^{25}	328.1	354.0	201.0
200 Mrad	632.0	683.0	664.6	500.1	517.5	582.6	1.1×10^{39}	3.3×10^{40}	8.2×10^{45}	461.7	490.3	593.5

TABLE-2

Function	Equation ($g(\alpha) = kt$)	Rate controlling process
D_1	$\alpha^2 = kt$	One dimensional diffusion (Parabolic law)
D_2	$(1-\alpha)\ln(1-\alpha) + \alpha = kt$	Two dimensional diffusion, cylindrical symmetry
D_3	$[1-(1-\alpha)^{1/3}]^2 = kt$	Three dimensional diffusion, spherical symmetry (Jander equation)
D_4	$(1-2/3\alpha) - (1-\alpha)^{2/3} = kt$	Three dimensional diffusion, spherical symmetry (Ginstiling Brownshtein equation)
F_1	$-\ln(1-\alpha) = kt$	Random nucleation; one nucleus on each particle (Mampel equation)
A_2	$[-\ln(1-\alpha)]^{1/2} = kt$	Random nucleation (Avrami equation I)
A_3	$[-\ln(1-\alpha)]^{1/3} = kt$	Random nucleation (Avrami equation II)
R_2	$1-(1-\alpha)^{1/2} = kt$	Phase boundary reaction; cylindrical symmetry
R_3	$1-(1-\alpha)^{1/3} = kt$	Phase boundary reaction; spherical symmetry

The decrease in energy of activiaion may arise due to two factors: (a) the chemical damage, and (b) extended lattice defects, both caused by irradiation. Here there is no evidence for chemical damage. Therefore, the decrease in E and ΔS^* values may be due to lattice defects.

Mechanism of thermal decomposition of zinc oxalate (both irradiated and unirradiated) was deduced by using non-isothermal method suggested by Sestak and Berggren[14] and Satava[15]. The types of mechanism most frequently encountered are given in Table-2. Thus, log $g(\propto)$ plotted against 1/T using $g(\propto)$ function are given in the above table by least square linear regression method.

Thermal decomposition of unirradiated as well as irradiated zinc oxalate followed F_1 mechanism *i.e.*, Mampel model equation, with ln $(1 - \propto)$ for $g(\alpha)$. The rate controlling process is random nucleation with the formation of a nucleus on every particle. Thus, irradiation did not cause any change in mechanism.

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