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NOTE

Kinetics and Mechanism of Thermal Decomposition of γ-Irradiated Manganese Oxalate

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The thermal decomposition of γ-irradiated manganese oxalate was studied by dynamic thermogravimetry. Kinetic parameters were calculated and the values were compared with those of unirradiated sample. The E, Z and ΔS* values decreased, reached a minumum and increased with increasing doses of radiation. The effect of γ-irradiation on the mechanism of decomposition was also studied. The mechanism is found to be changing on irradiation.

When substances are irradiated with ionizing radiation it may result in a variety of physical and chemical changes, which depend on the nature of the system and the energy of the incident radiation. Irradiation often creates new potential nucleation centres. The changes occurring may be either electronic or structural.

A number of studies have been made on the effect of irradiation on oxalates[1–5]. The rate constants for accelerating and decay stages are found to be enhanced in isothermal decomposition. The formation and growth of nucleation centres due to chemical and lattice defects created by irradiation are found to affect the kinetic parameters and mechanism of the reaction.

Manganese oxalate dihydrate was prepared by treating hot solutions of manganese sulphate with potassium oxalate. The substance with particle size in the range 90–106 microns was irradiated with Co-60 γ-radiation at room temperature. The samples were taken in glass ampoules and four doses, *viz.*, 50 Mrad, 100 Mrad, 150 Mrad and 200 Mrad were given to four samples respectively. Dose rate was 0.07 Mrad/h. The non-isothermal TG of four samples along with one unirradited sample were taken in static air atmosphere with a heating rate of 5 K per min using Shimadzu thermal analyser.

The decomposition of $MnC_2O_4 \cdot 2H_2O$ occurs in two stages:

$$MnC_2O_4 \cdot 2H_2O \longrightarrow MnC_2O_4 + 2H_2O$$

$$MnC_2O_4 \longrightarrow MnO + CO + CO_2$$

The effect of γ-irradiation on the second stage of decomposition is studied here. The Coats-Redfern (CR) method[6] was used for calculating the kinetic parameters such as activation energy E, frequency factor Z and entropy of activation ΔS* which are given in Table-1.

TABLE-1
EFFECT OF γ-IRRADIATION ON KINETIC PARAMETERS OF MANGANESE OXALATE

Static air atmosphere; heating rate: 5 k min^{-1}; mass of the sample in each case: 10 mg

Dose [Mrad]	Order [n]	T_i	T_f	T_s	E [kJ mol^{-1}]	Z [s^{-1}]	ΔS* [J K^{-1} mol^{-1}]
Unirradiated	1	493.5	593.4	542.0	781.4	3.22×10^{62}	946.7
50	0	493.4	593.0	542.3	551.2	3.57×10^{43}	583.8
100	0	493.3	593.1	540.7	389.5	2.15×10^{35}	426.5
150	0	493.4	593.1	543.8	278.4	1.72×10^{24}	213.9
200	0	493.5	593.1	545.6	486.7	1.34×10^{44}	594.8

When compared to unirradiated samples the procedural temperature of initiation of decomposition T_i and final temperature of decomposition T_f remained more or less the same. Temperature of maximum decomposition T_s showed an increase except in the case of the sample, which was subjected to a dose of 100 Mrad. The E, Z and ΔS* showed decrease, reached a minimum for 100 Mrad and then increased (Fig. 1). This result is similar to the one obtained in the study of thermal decompositon of γ-irradiated zinc oxalate dihydrate[7].

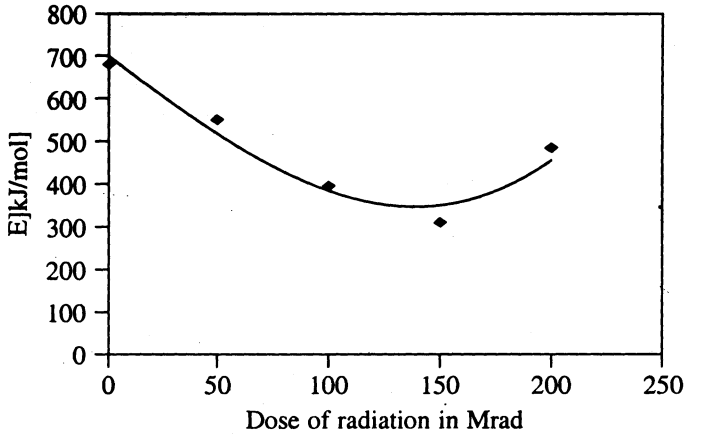

Fig. 1. Effect of γ-radiation on energy of activation

The chemical damage as well as extended lattice defects, both caused by γ-irradiation may result in decrease with energy of activation. Here no chemical changes were observed due to the γ-irradiation. Therefore, the decrease in E and ΔS* values is 7 due to lattice defects.

The method suggested by Sesthak and Berggren[8] and Satava[9] was used for deducing the mechanism of thermal decomposition of irradiated as well as unirradiated manganese oxalate.

Thermal decomposition of unirradiated manganese oxalate followed F_1 mechanism, *i.e.*, Mampel model equation. The rate controlling process is random nucleation with the formation of a nucleus on every particle. The samples which

were subjected to a dose of 50 Mrad and 200 Mrad followed R_3 mechanism [phase boundary reaction with spherical symmetry] and those subjected to 100 Mrad and 150 Mrad followed R_2 mechanism [phase boundary reaction with cylindrical symmetry].

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