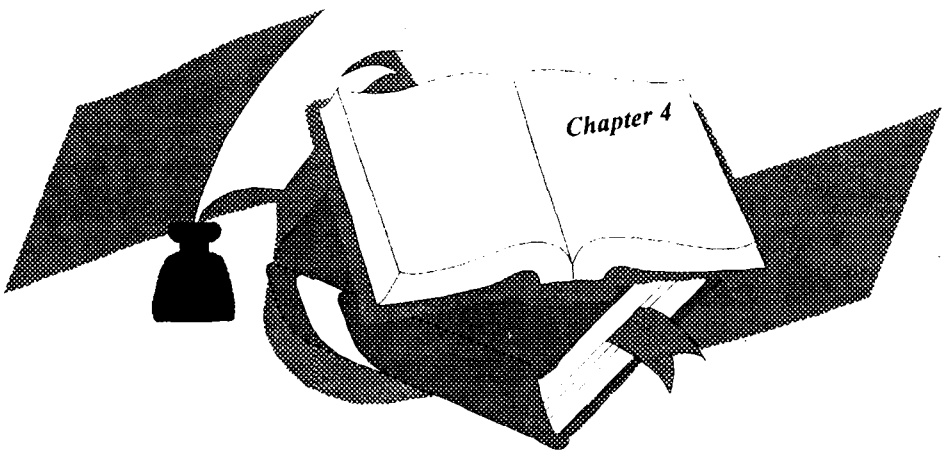
Chapter 4



CHAPTER IV

EFFECT OF OXIDE ADDITIVES ON THERMAL DECOMPOSITION OF STRONTIUM OXALATE

4.1 EXPERIMENTAL ASPECTS

The effect of zinc and copper oxide additives on the thermal decomposition of strontium oxalate was investigated using both dynamic and isothermal TGA in air. Similarly the effect of γ -irradiation on the thermal decomposition of strontium oxalate with oxide additives was studied. The details of preparation and irradiation of sample; recording of dynamic and isothermal TGA of binary mixture of strontium oxalate and oxides are described below.

4.1.1 Preparation of Sample

The BDH grade zinc oxide and copper oxide were used as additives. Anhydrous strontium oxalate, zinc oxide and copper oxide were passed through 200 mesh size. The binary mixtures containing a fixed composition of 10% by weight of oxide were prepared by physical incorporation of metal oxide in oxalate. 200 mesh size crystals of both strontium oxalate (90% by weight) and zinc oxide (10% by weight) were weighed accurately and then mixed mechanically in a agate mortar. It is an admixture of oxalate and oxide having a fixed composition which was verified by usual analytical methods **[149]**. Strontium oxalate 90% by weight and copper oxide 10% by weight were mixed in a similar way.

4.1.2 Irradiation of Samples

The known weights of binary mixtures of strontium oxalate and oxides were transferred to glass ampoules and sealed. The tubes were wrapped in black paper to protect them from external light. These sample tubes were exposed to different doses using a 60 Co γ - Source. The irradiated binary mixtures of oxalate and oxides were subjected to dynamic and isothermal TGA.

4.1.3 Dynamic and Isothermal TGA

50 mg of binary mixture of oxalate and oxide, immediately after removal from the gamma source, was transferred to a quartz cup of the TGA apparatus. The weight loss of the sample in dynamic TGA was recorded on a thermobalance from room temperature to 600°C at a rate of 5°C per minute.

The binary mixture of oxalate and oxide, after receiving a predetermined gamma dose, was transferred in a quartz tube and weighed accurately upto 50 mg on a thermobalance. The weight loss of the sample was recorded at a constant temperature in isothermal TGA with time. The isothermal TGA of binary mixtures were scanned in the temperature range of 490 to 530°C at an interval of 10°C..pa

4.1.4 Kinetic Parameters

In order to evaluate the kinetic parameters, the plots of percentage weight loss versus temperature were obtained from dynamic TGA data of all the binary mixtures. The energy of activation, f(α), ln(A) are evaluated using the Coats-Redfern equation [Eqn.No.2.5] **[156]**. Similarly, the α -time plots were obtained from isothermal TGA studies. The rate constant, the energy of activation and lnA value were determined using the kinetic rate expressions.

4.2 RESULTS

The data obtained from dynamic TGA and isothermal TGA containing 10% zinc oxide and copper oxide in binary mixtures of strontium oxalate is analysed. Similarly,the kinetic parameters were evaluated for binary mixtures at each absorbed doses.

4.2.1 Dynamic TGA of Binary Mixtures

The thermograms obtained for dynamic TGA of unirradiated binary mixtures of oxalate containing each 10% by weight zinc oxide and copper oxide are shown in Fig. 4.1. The Arrhenius plots of f(α) vs 1/T are shown in Fig. 4.2 (a). The data on percentage weight loss, decomposition temperature, energy of activation for thermal decomposition of unirradiated binary mixtures are presented in Table 4.1. An important observation is that the onset temperature of decomposition of pure strontium oxalate of oxide is 470°C. This temperature decreases from 470°C to 460° and 445°C on addition of zinc and copper oxide as additives respectively. The energy of activation decreases by 50% when zinc oxide is added to the binary mixture while it reduces to 30% in presence of copper oxide additive.

4.2.2 Dynamic TGA of Irradiated Binary Mixture

The plots of percentage weight loss vs temperature for dynamic TGA of irradiated binary mixtures containing zinc and copper oxides are shown in Fig. 4.3 and Fig. 4.4 respectively. The Arrhenius plots of f(α) versus 1/T for irradiated binary mixtures containing Zn and Cu oxides are shown in Fig. 4.2(b). The slope of these Arrhenius plots showed a decreasing trend with increasing absorbed dose. The data on decomposition temperature energy of activation and lnA values for irradiated binary mixtures of strontium oxalate and oxides is summarised in Tables 4.2 and 4.3. The effect of radiation on energy of activation for binary mixture can be represented by plotting a graph of Ea *versus dose* (Fig. 4.5). The energy of activation sharply decreases [Fig 4.5a] at very low dose, when zinc oxide is present in strontium oxalate as an additive. On the other hand, the energy of activation showed increase [Fig.4.5b] at a lower in case of dynamic TGA of strontium oxalate with copper oxide additivies. The same trend was observed for dynamic TGA of unirradiated pure strontium oxalate (Fig. 2.10).

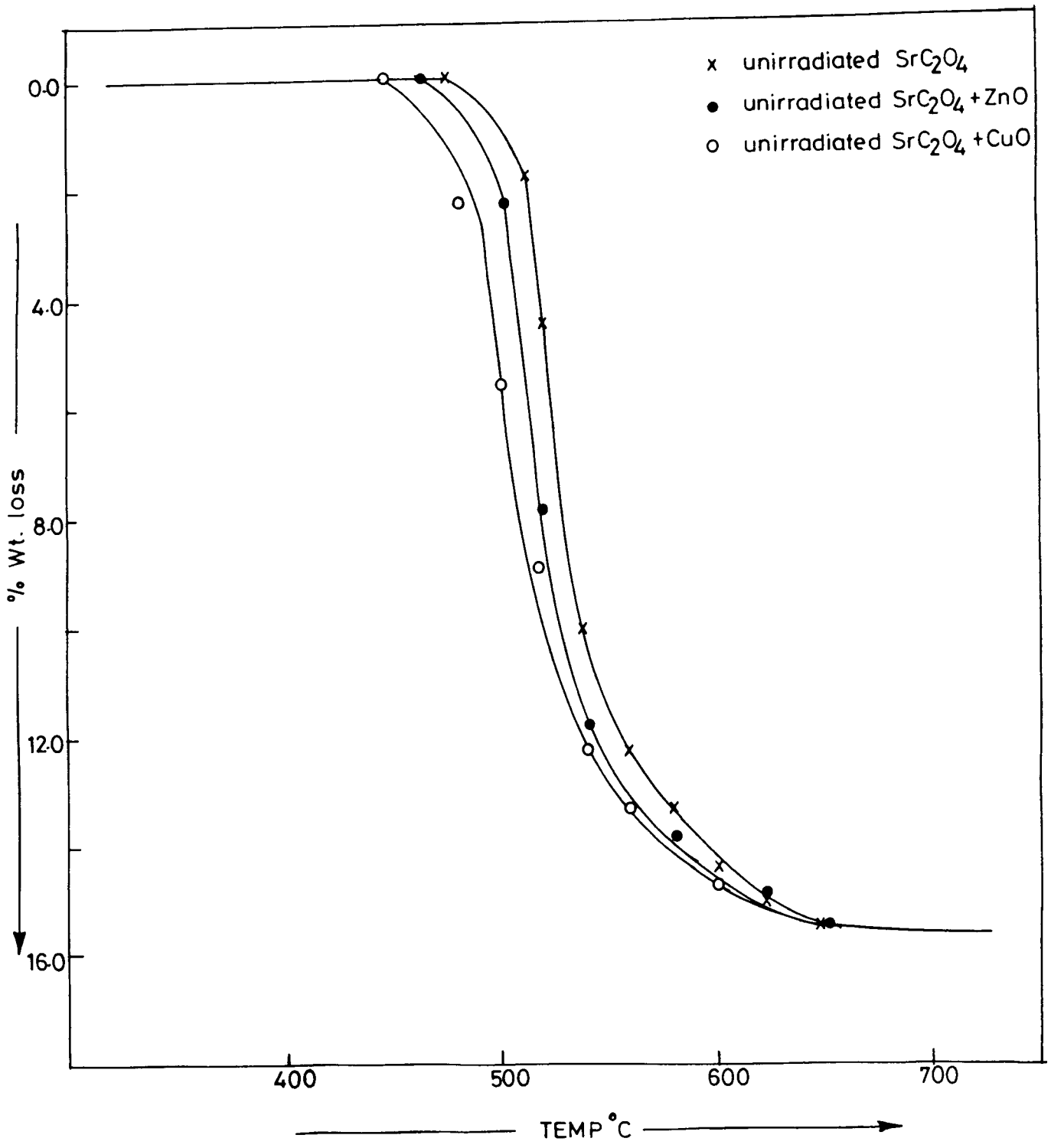


Fig. 4.1 : Dynamic TGA of

1) unirradiated SrC_2O_4.

2) unirradiated SrC_2O_4 + ZnO (10%)

3) unirradiated SrC_2O_4 + CuO (10%)

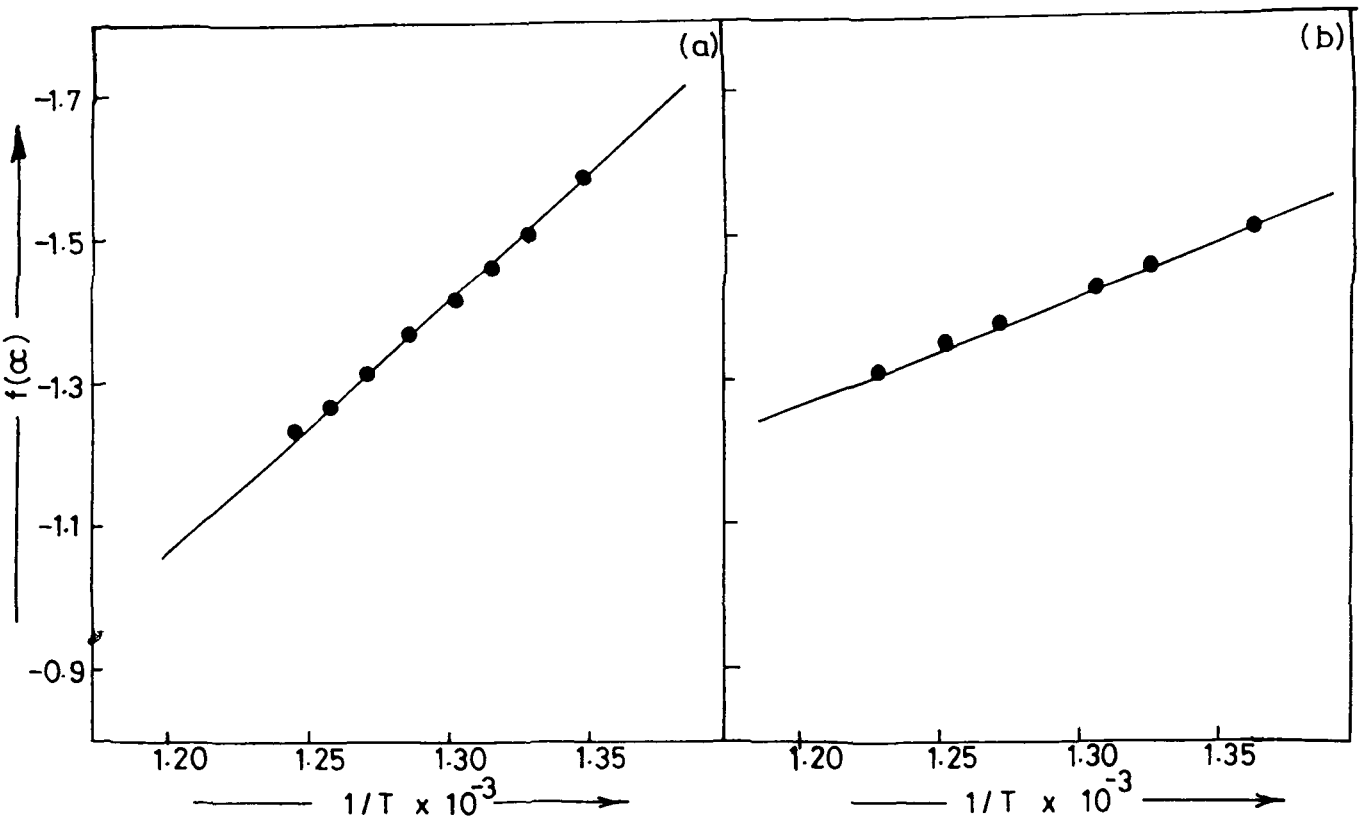


Fig.4.2 (a) : f(α) vs 1/T plots form dynamic TGA of unirradiated (a) SrC_2O_4 + ZnO (b) SrC_2O_4 + CuO.

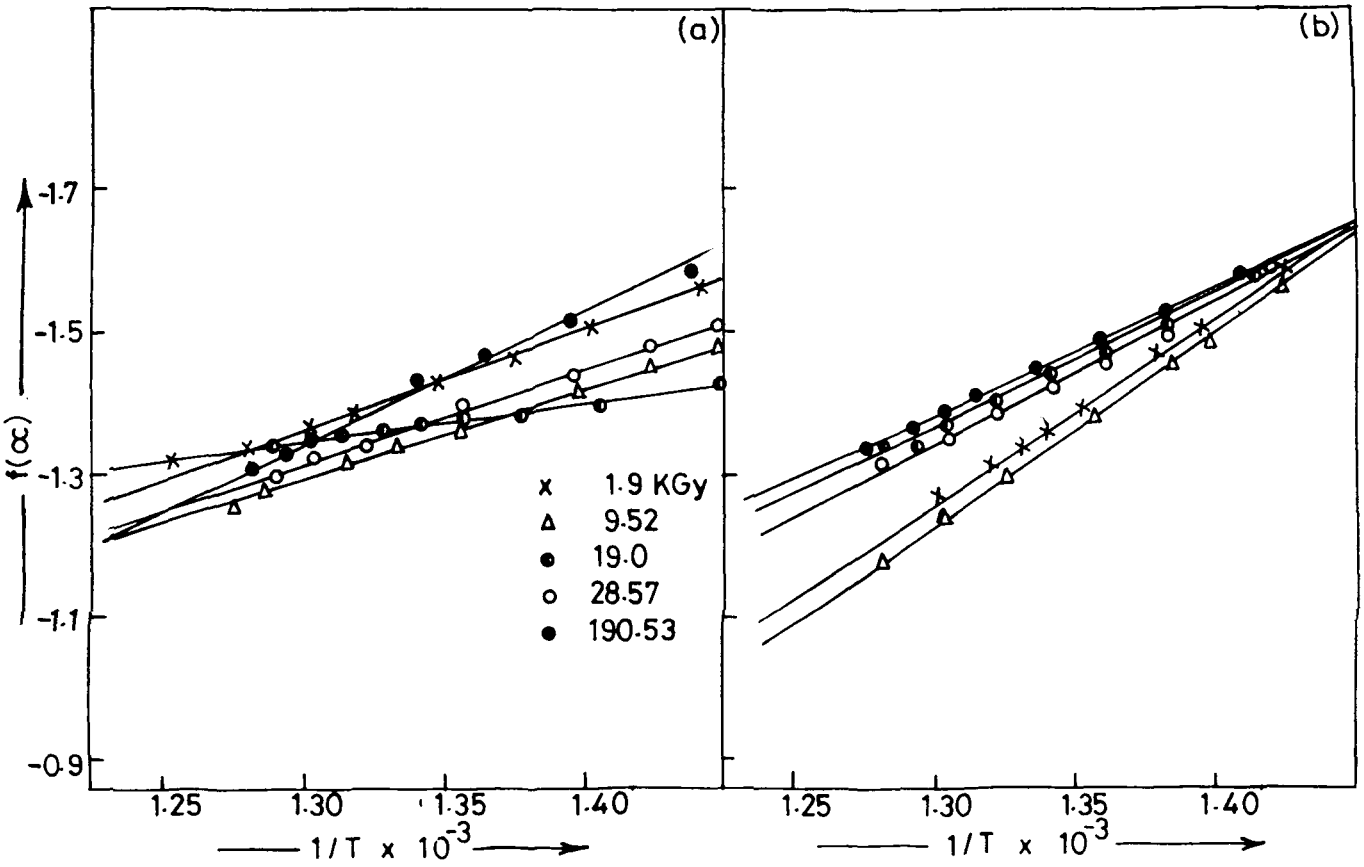


Fig.4.2 (b): f(α) vs 1/T plots form dynamic TGA of γ-irradiated (a) SrC_2O_4 + ZnO (b) SrC_2O_4 + CuO.

Table 4.1 : Kinetic data of dynamic TGA of ZnO and CuO additives of strontium oxalate

Name of the compound	Percentage weight loss		Decomposition temperature range ($T^{\circ}C$)	Energy of activation Ea (kJ/mol)
	Calculated	*Observed*		
SrC_2O_4	15.94	15.7	470-540	369.4 ± 4
SrC_2O_4 (90%) + ZnO (10%)	15.94	15.6	460.540	184.0 ± 2
SrC_2O_4 (90%) + CuO (10%)	15.94	15.6	445-535	113.0 ± 1

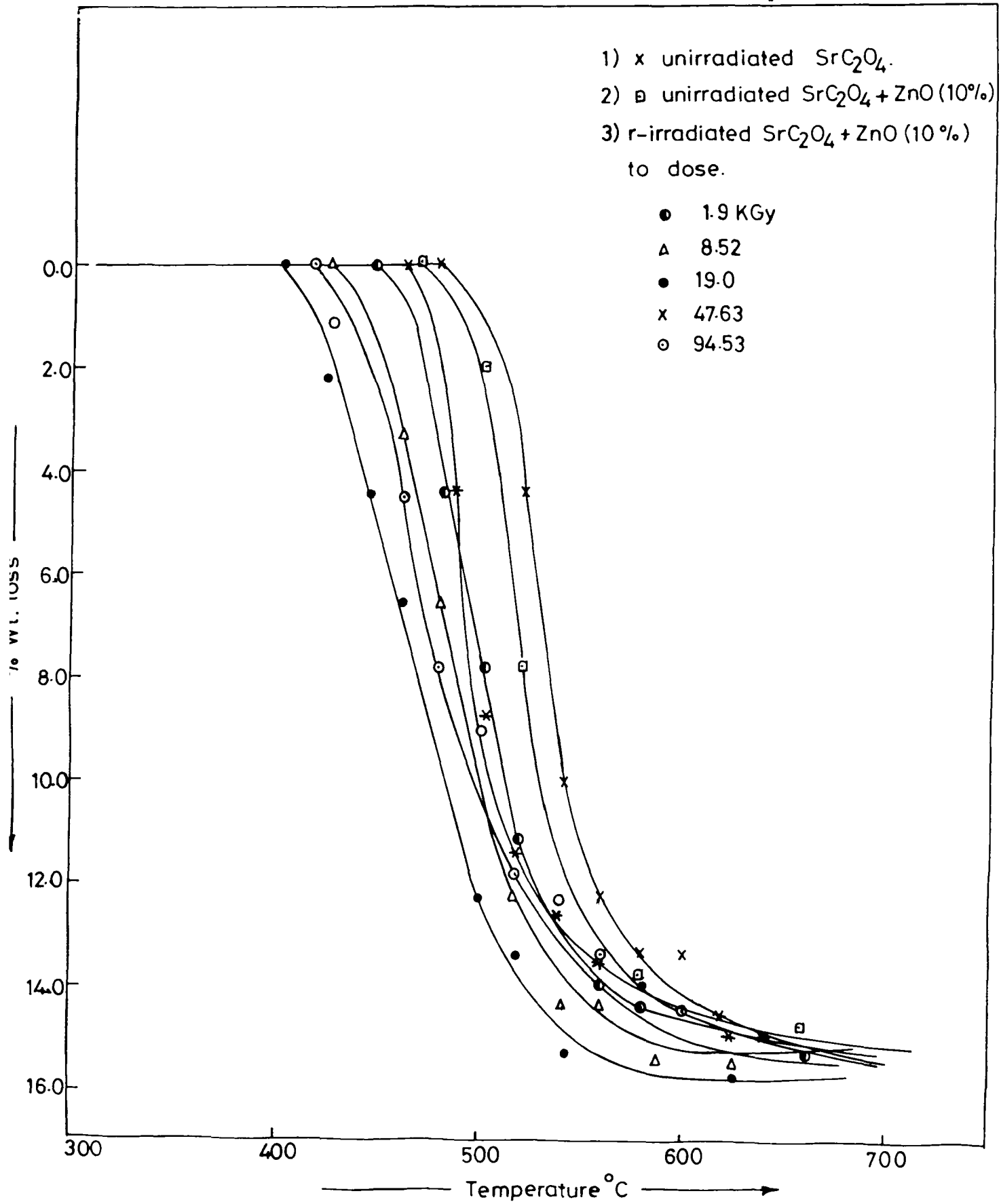


Fig. 4.3 : Dynamic TGA of γ - irradiated SrC_2O_4 + ZnO (10%)

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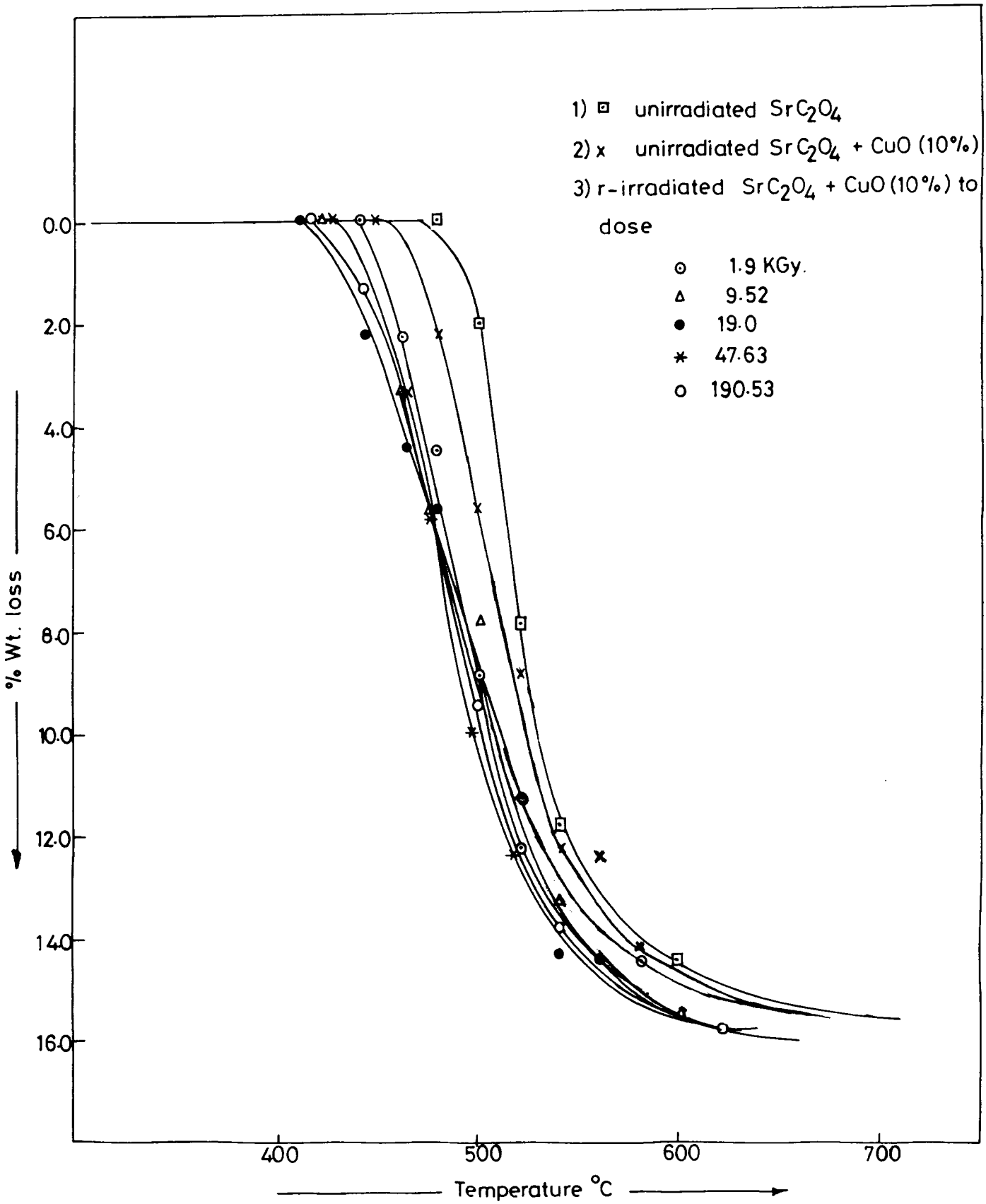

Fig. 4.4 : Dynamic TGA of γ - irradiated SrC_2O_4 + CuO (10%)

Table 4.2 : Kinetic data of dynamic TGA of iraidated strontium oxalate + 10% zinc oxide samples

Corrected irradiated dose absorbed (KGy)	Decomposition temperature range ($T^{o}C$)	In A	Energy of activation Ea (kJ/mol)
0.0	460-580	24.59	184.0 ± 2
1.9	440-560	10.39	113.3 ± 1
9.5	420-540	10.41	104.9 ± 1
19.0	400-530	10.53	109.8 ± 1
47.6	455-550	8.89	105.6 ± 1
190.5	415-550	10.28	113.7 ± 1

Table 4.3 : Kinetic data of dynamic TGA of irradiated strontium oxalate + 10% copper oxide samples.

Corrected irradiated dose absorbed (KGy)	Decomposition temperature range ($T^{o}C$)	In A	Energy of activation Ea (kJ/mol)
0.0	445-560	8.17	113.0 ± 1
1.9	435-530	29.28	227.0 ± 2
9.5	420-540	22.61	177.8 ± 2
19.0	410-540	16.62	152.8 ± 2
47.6	425-545	14.39	137.6 ± 1
190.5	415-540	12.99	130.0 ± 1

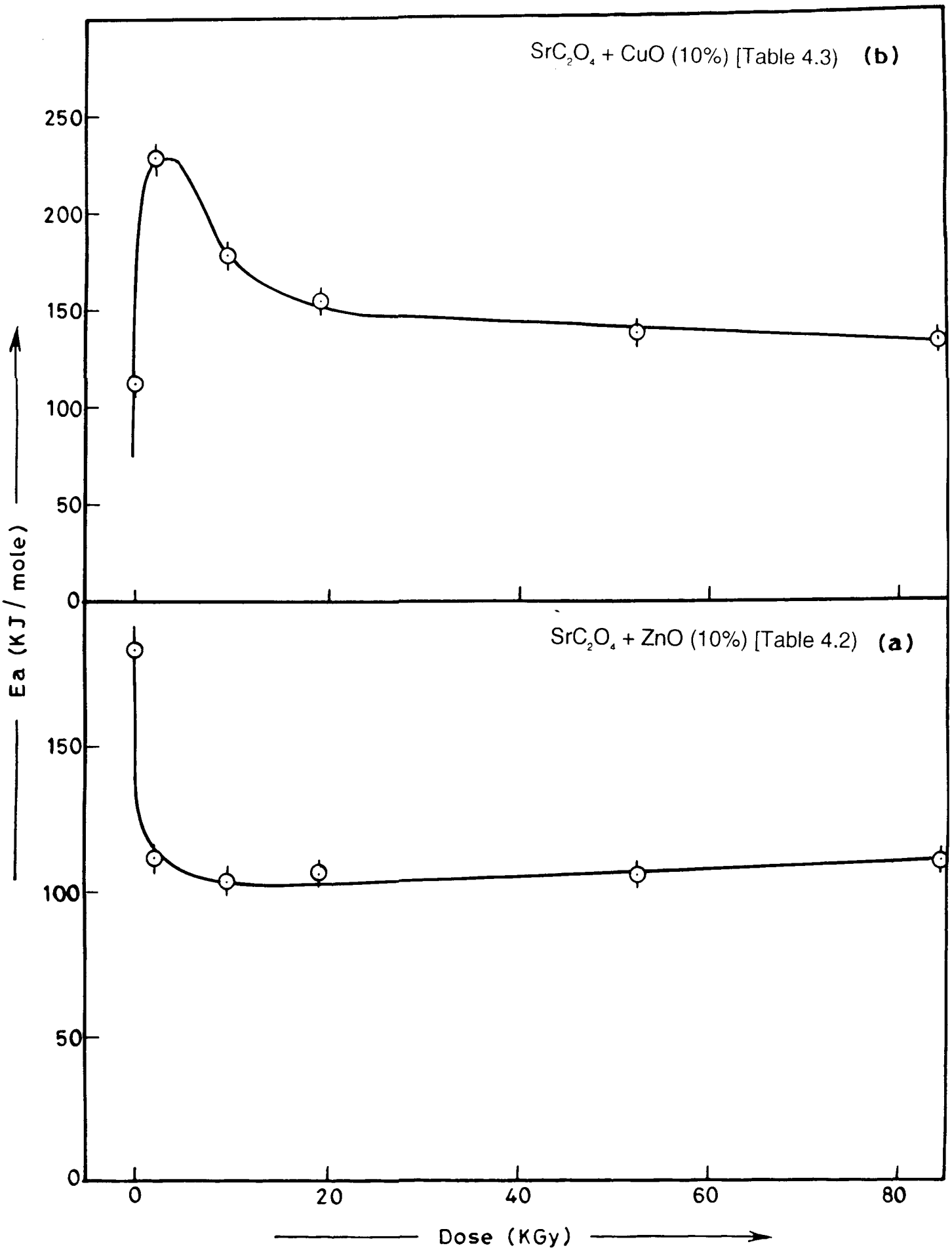

Fig. 4.5 : Plots of Ea vs dose of γ - irradiated (a) SrC_2O_4 + ZnO (b) SrC_2O_4 + CuO from dynamic TGA

4.2.3 Isothermal TGA of Binary Mixture

The values are calculated for isothermal TGA of binary mixtures by using equation 3.1. The half decomposition reaction time ($t_{0.5}$) is obtained for binary mixtures containing zinc and copper oxide respectively, from the plots of versus time, shown in Figs. 4.6a and 4.7a. The plots of α versus $t/t_{0.5}$ for zinc and copper oxide additives are shown in Figs. 4.6b and 4.7b respectively. The nature of this master plot is almost identical to the similar plot obtained for isothermal decomposition of pure strontium oxalate. The $f(\alpha)$ values for the best fit mechanistic equation are taken from Table 3.1. The linear plots of $f(\alpha)$ versus time for zinc and copper oxide additives are shown in Figs. 4.6c and 4.7c respectively.

The slopes of these plots give the values of the rate constants K. The Arrhenius plots of lnk versus 1/T for zinc and copper oxide additives are shown in Figs. 4.6d and 4.7d respectively. The energy of activation and lnA values were determined from the Arrhenius plots. The kinetic data for the isothermal TGA of binary mixtures is summarised in Table 4.4.

4.2.4 Isothermal TGA of Irradiated Binary Mixtures

Isothermal TGA of binary mixtures irradiated to various doses are obtained. The plots of α versus time, α versus $t/t_{0.5}$, $f(\alpha)$ versus time and lnk versus 1/T are obtained for irradiated binary mixture of strontium oxalate containing 10% zinc oxide. These plots are shown from Fig. 4.8 to Fig. 4.13. Similarly plots for isothermal TGA of irradiated strontium oxalate containing 10% copper oxide additive are shown in Fig. 4.14 to Fig. 4.19. The energy of activation for each dose absorbed is determined from the Arrhenius plots of lnk versus 1/T. The kinetic data for thermal decomposition of irradiated binary mixtures containing zinc and copper oxides are summarised in Tables 4.5 and 4.6 respectively. Fig. 4.20 shows the variation in energy of activation with absorbed dose for both the binary mixtures. The energy of activation exponentially decreases with

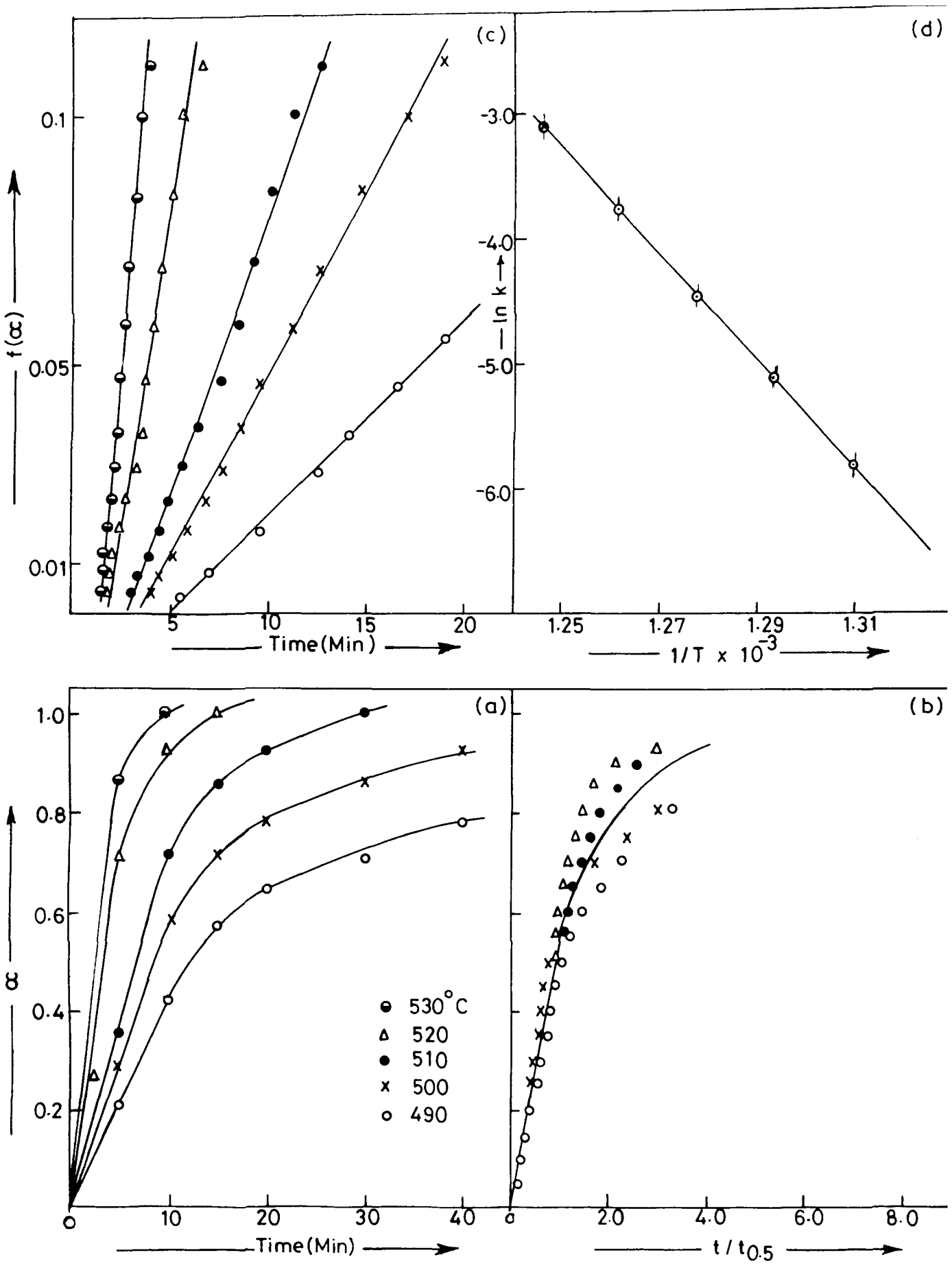

Fig. 4.6 : Isothermal TGA plots for unirradited SrC_2O_4 + ZnO (10%)

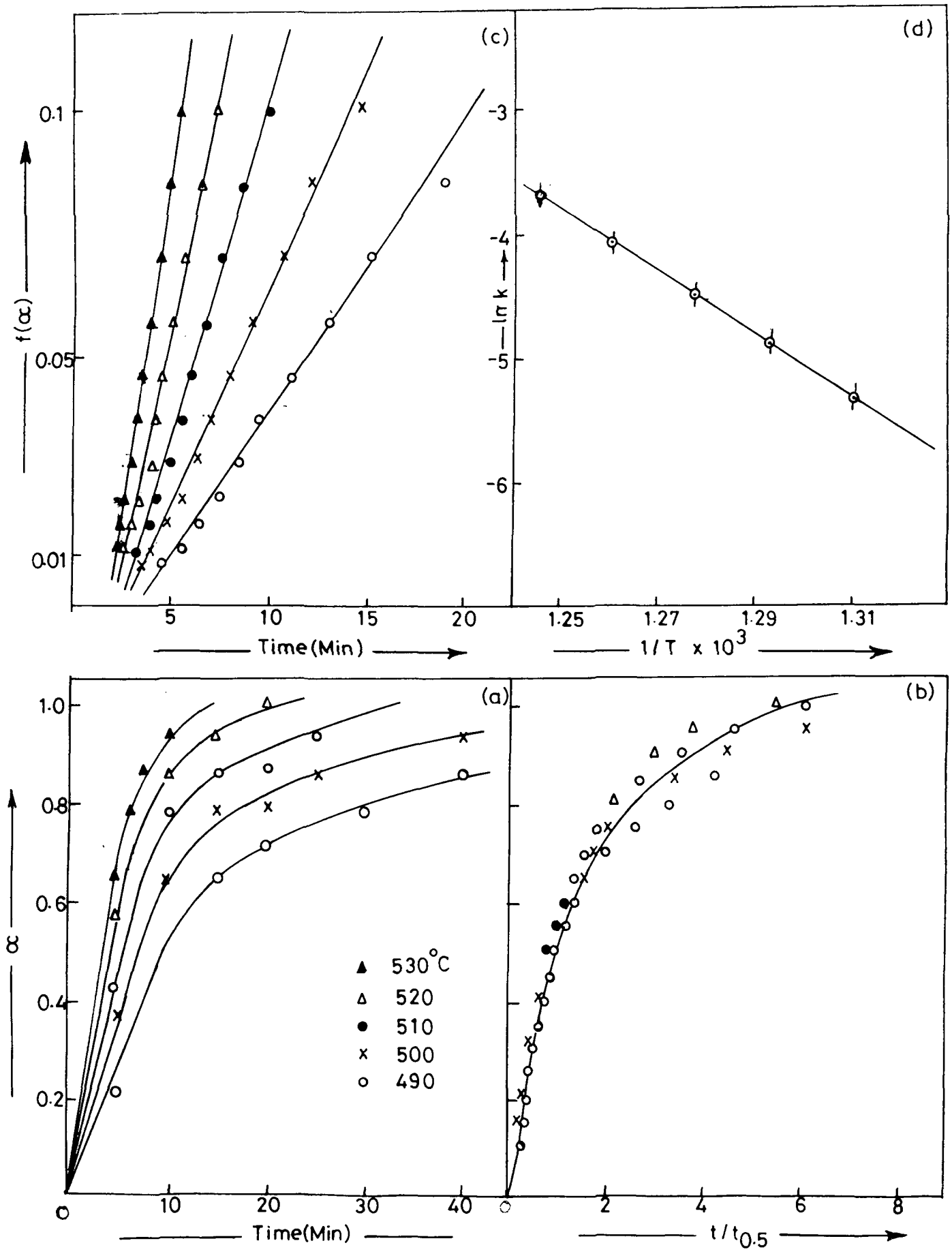

Fig. 4.7 : Isothermal TGA plots for unirradited SrC_2O_4 + CuO (10%)

Table 4.4 : Kinetic data of isothermal TGA of strontium oxalate in presence of ZnO and Cu additives.

Substance	Isothermal temperature ($T^{\circ}C$)	$1/T^{\circ}K \times 10^{-3}$	Rae constant $X10^{-3}(min^{-1})$	Ink	Intercept $X 10^{-2}$
Strontium oxalate + 10% ZnO	490	1.310	2.94	-5.83	-0.75
	500	1.293	5.97	-5.12	-1.19
	510	1.277	11.36	-4.48	-2.82
	520	1.261	23.47	-3.75	-3.18
	530	1.245	47.29	-3.05	-4.23
Ea = 238.0 kJ/mol ln A = 40.96					
Strontium oxalate + 10% CuO	490	1.310	4.58	-5.38	-0.87
	500	1.293	7.75	-4.86	-1.51
	510	1.277	10.23	-4.58	-1.25
	520	1.261	16.50	-4.10	-2.23
	530	1.245	24.69	-3.70	-2.71
Ea = 128.0 kJ/mol ln A = 22.98					

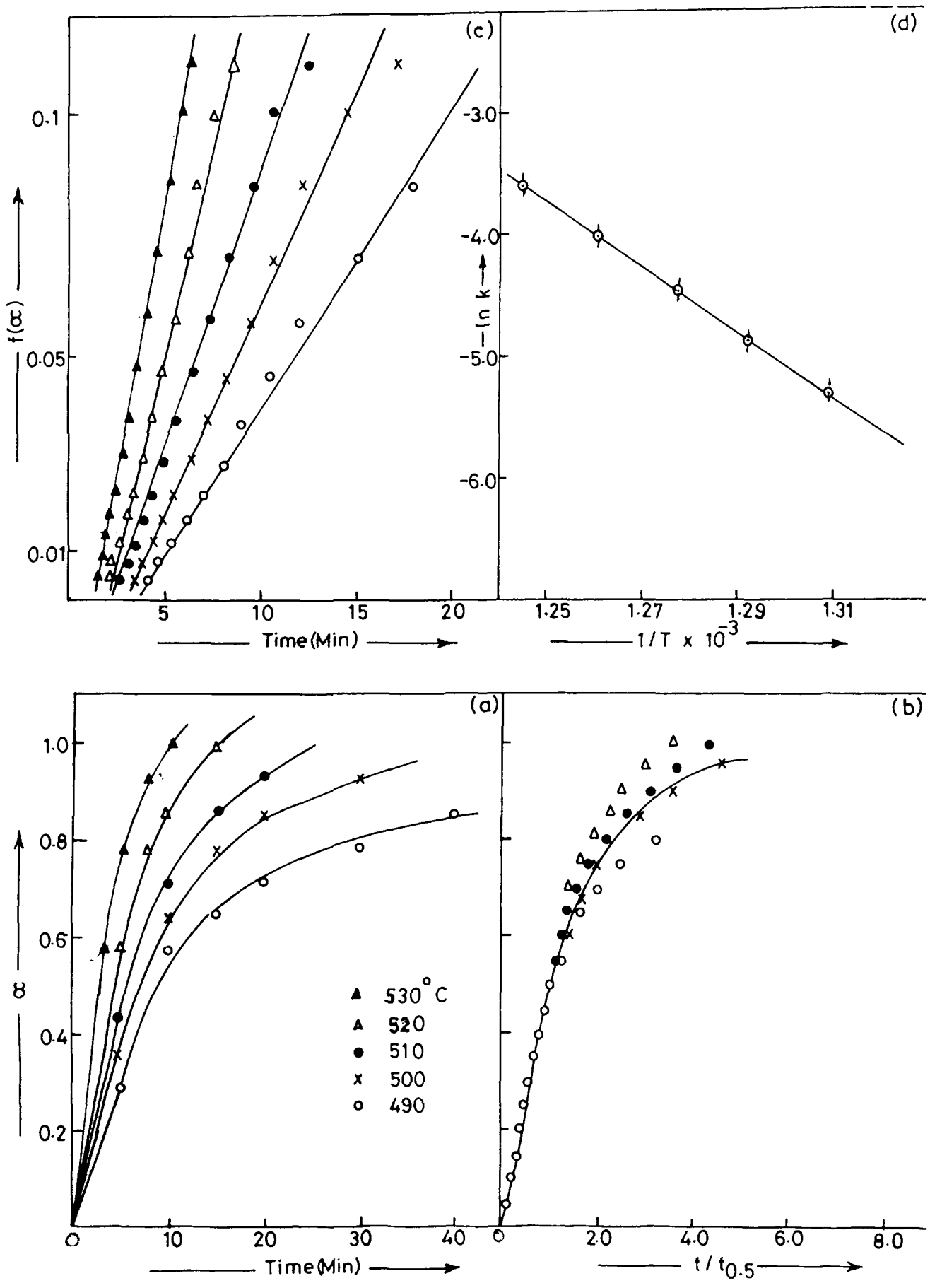

Fig. 4.8 : Isothermal TGA plots for γ - irradiated SrC_2O_4 + ZnO (10%) (dose = 1.9 KGy)

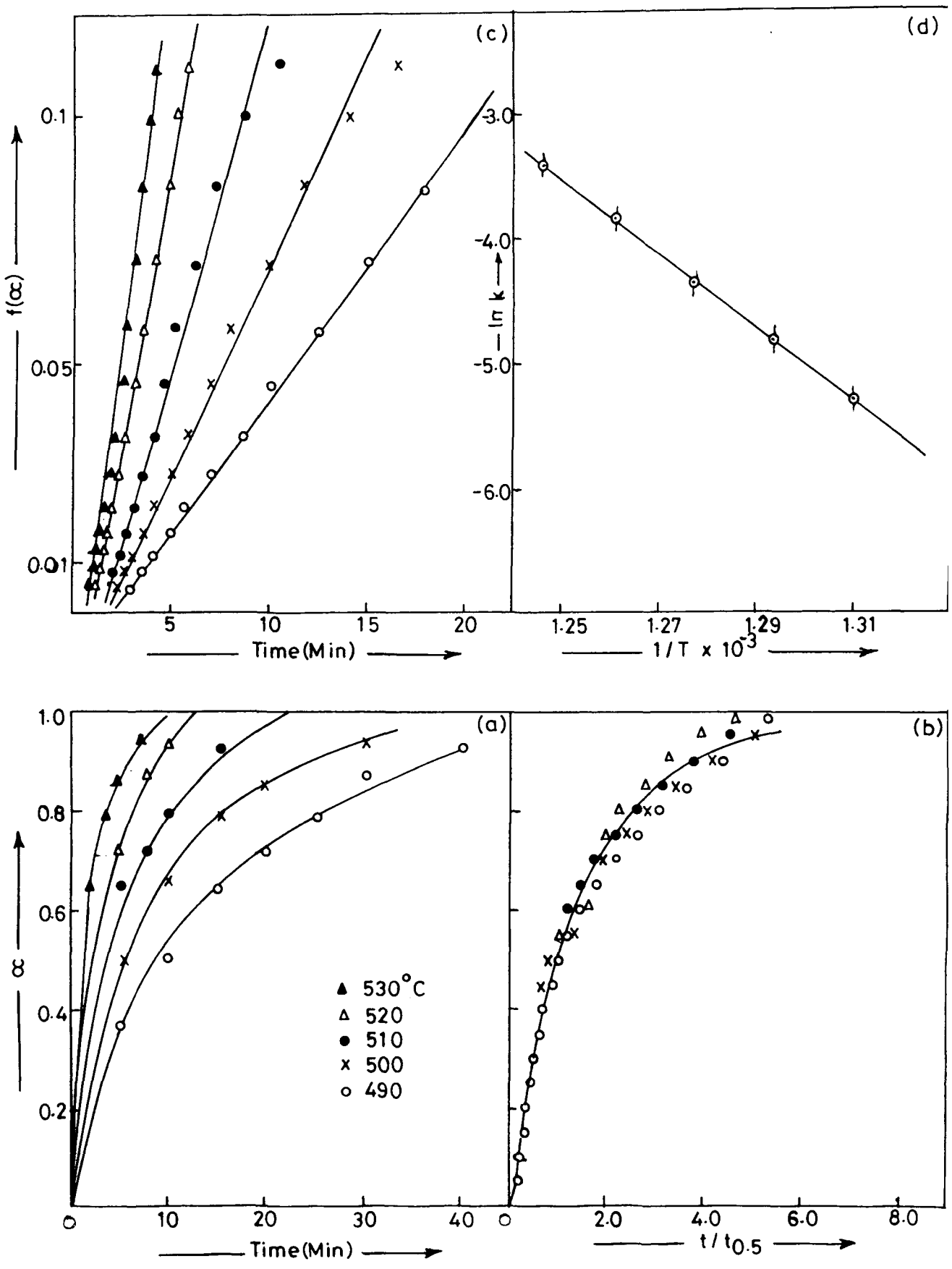

Fig. 4.9 : Isothermal TGA plots for γ - irradiated SrC_2O_4 + ZnO (10%) (dose = 7.6 KGy).

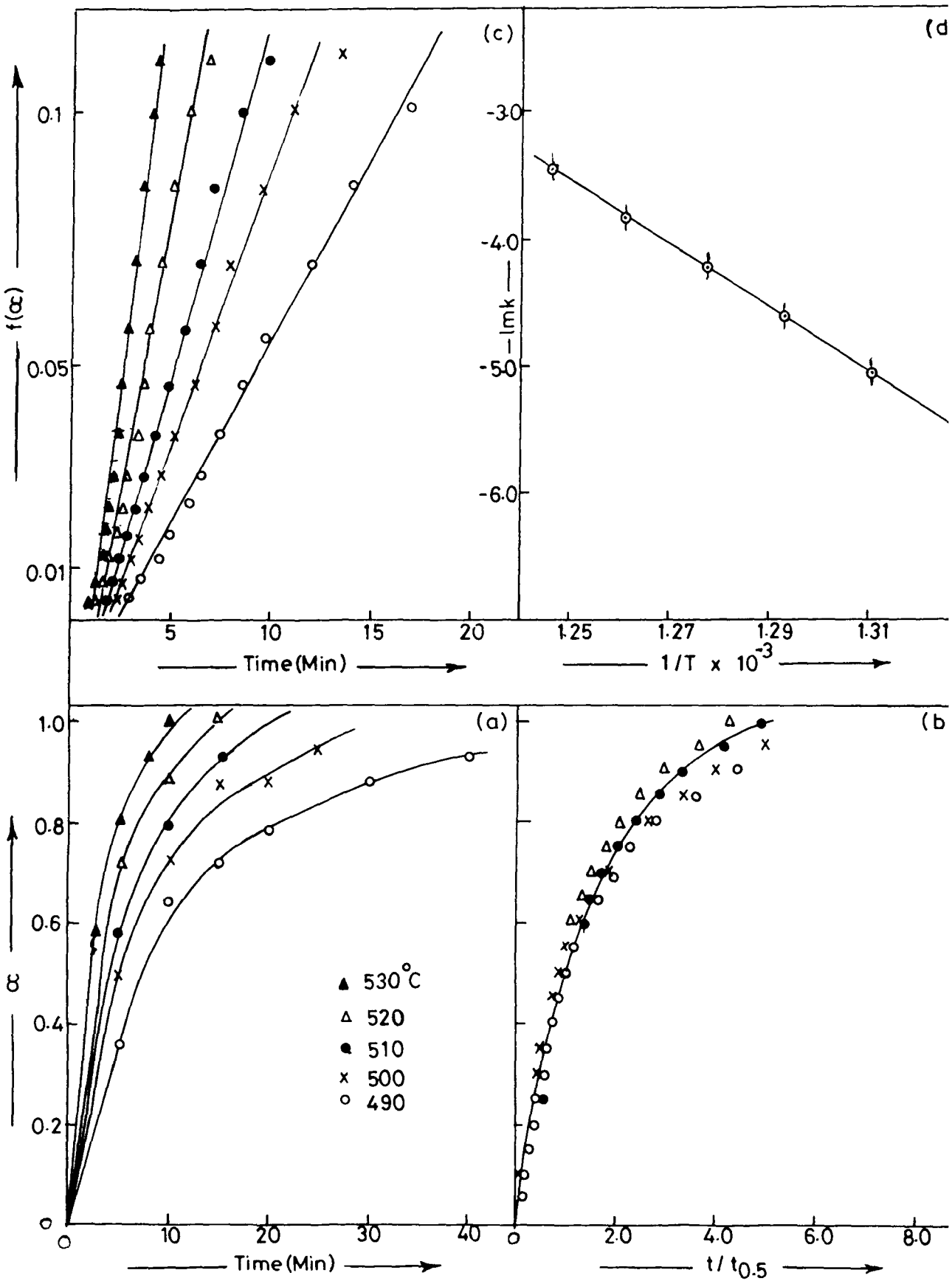

Fig. 4.10 : Isothermal TGA plots for γ -irradiated SrC_2O_4 + ZnO (10%) (dose = 13.3 KGy)

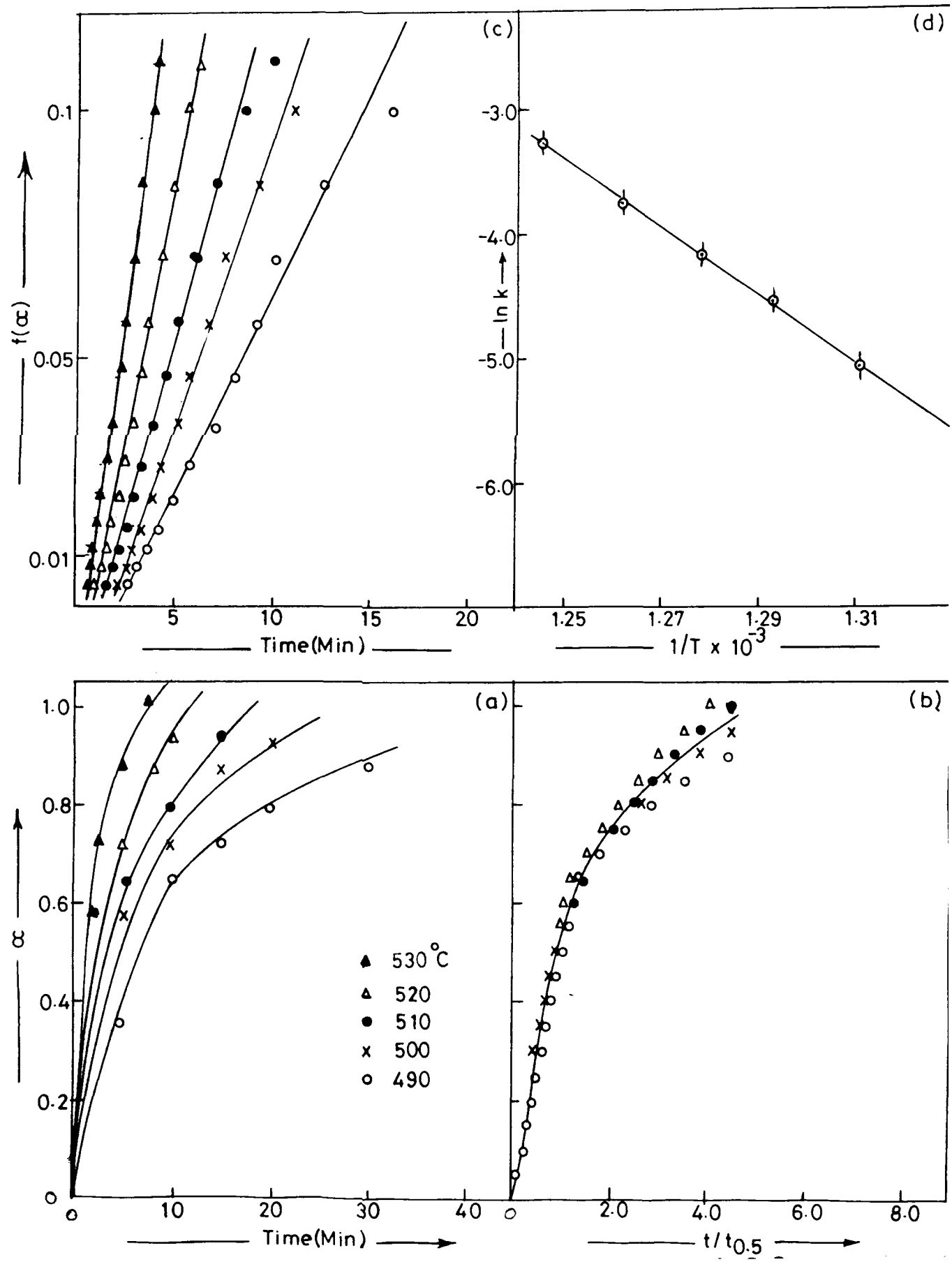

Fig. 4.11 : Isothermal TGA plots for γ -irradiated SrC_2O_4 + ZnO (10%) (dose = 19.0 KGy).

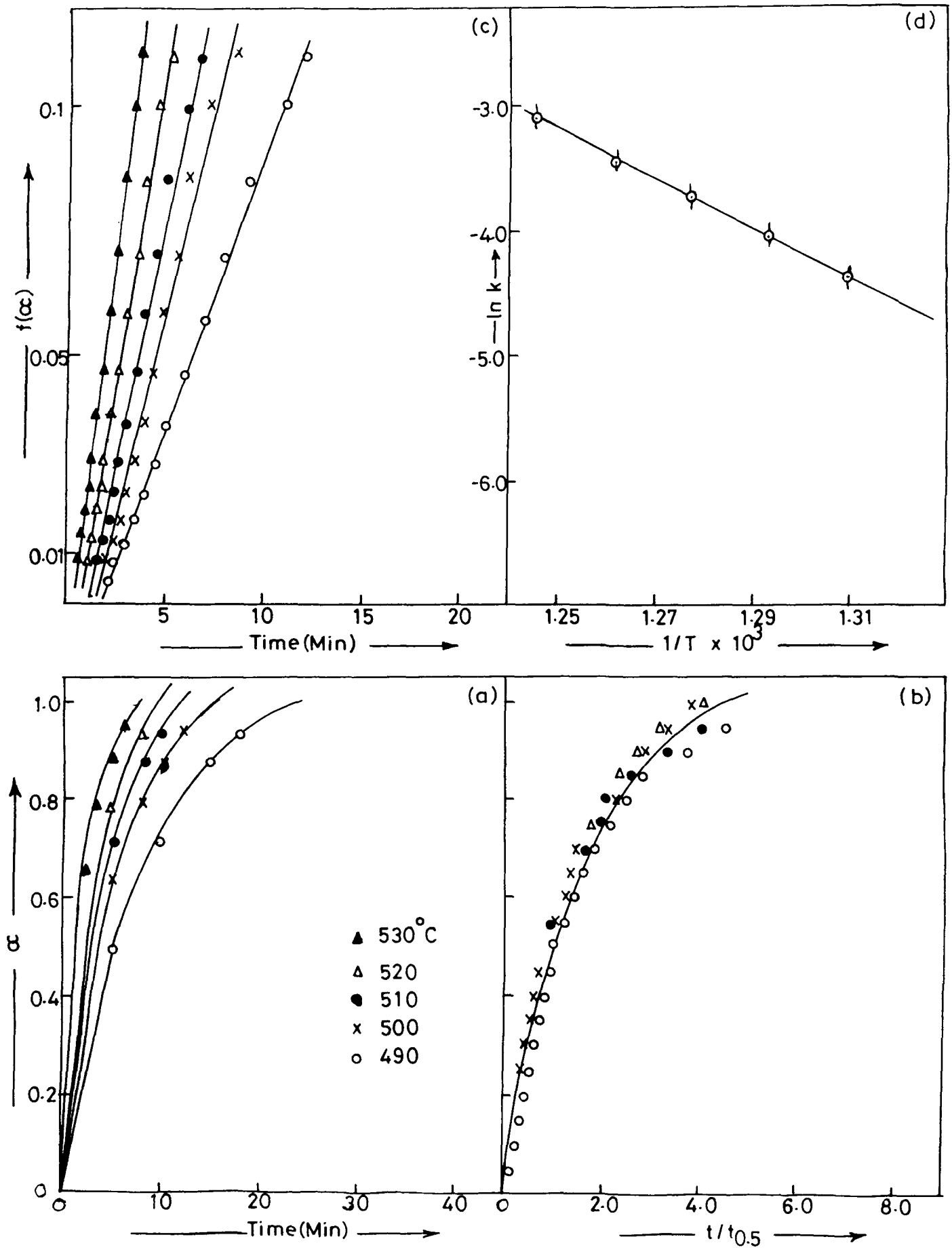

Fig. 4.12 : Isothermal TGA plots for γ -irradiated SrC_2O_4 + ZnO (10%) (dose = 38.0 KGy).

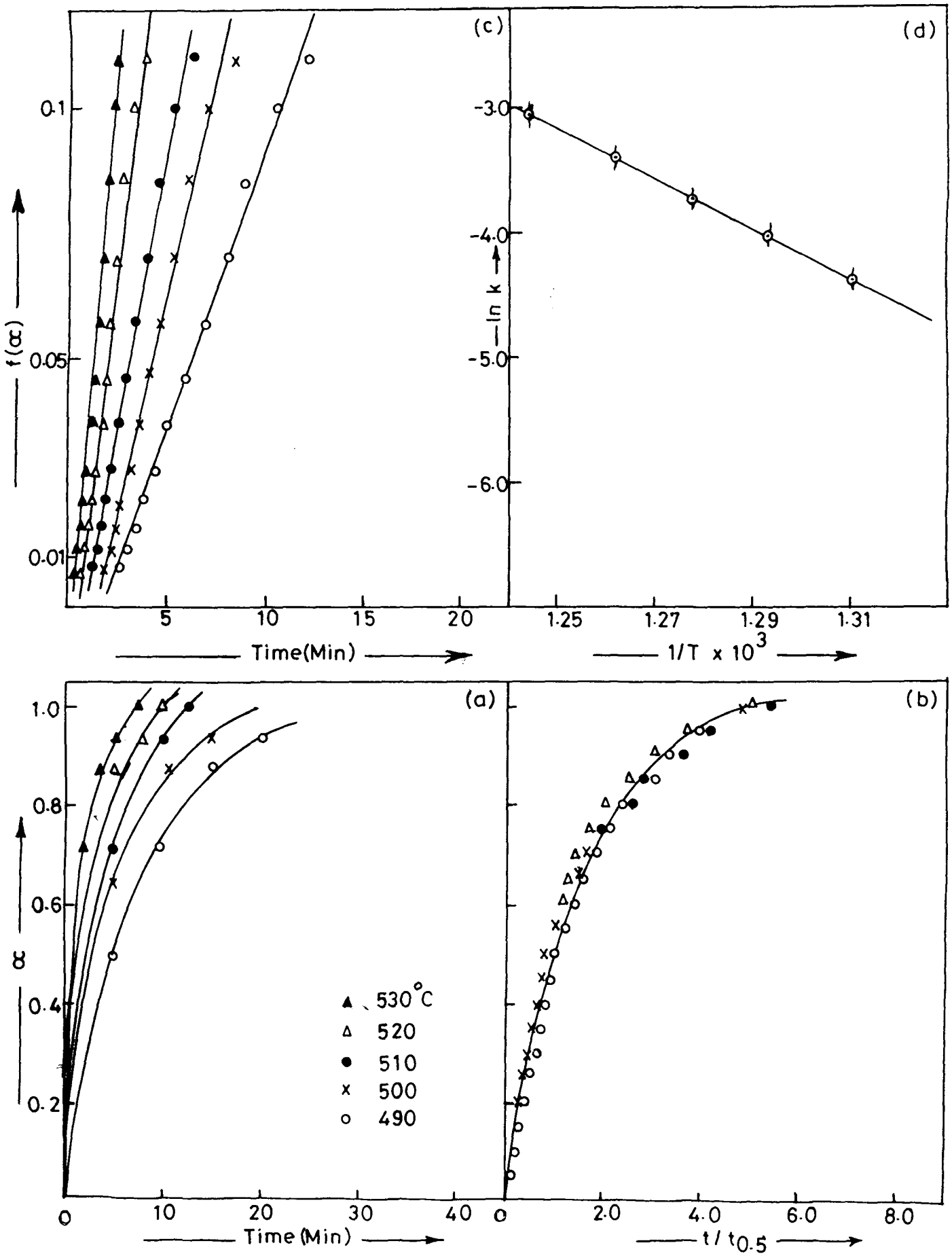

Fig. 4.13 : Isothermal TGA plots for γ -irradiated SrC_2O_4 + ZnO (10%) (dose = 18.2 KGy).

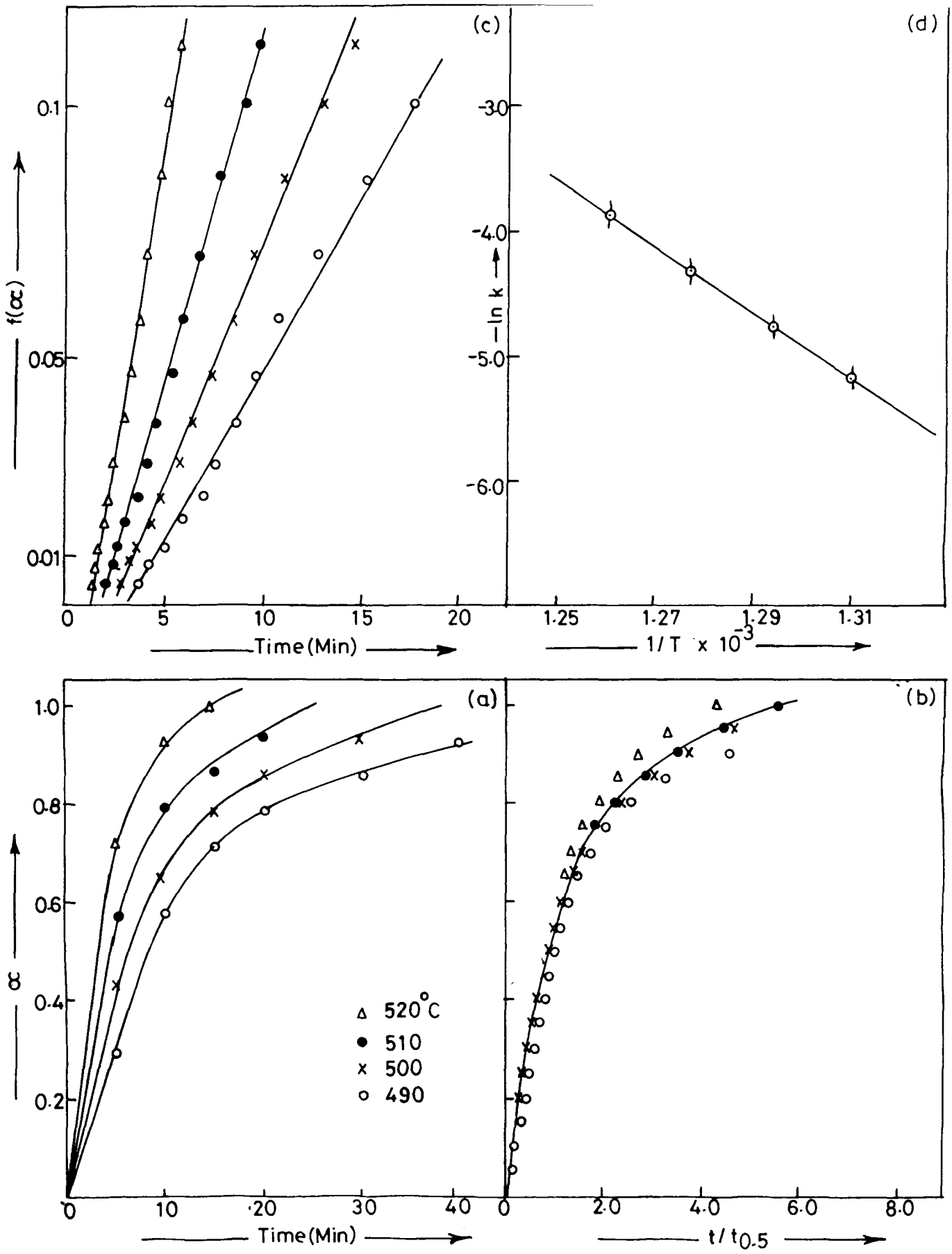

Fig. 4.14 : Isothermal TGA plots for γ -irradiated SrC_2O_4 + CuO (10%) (dose = 1.9 KGy).

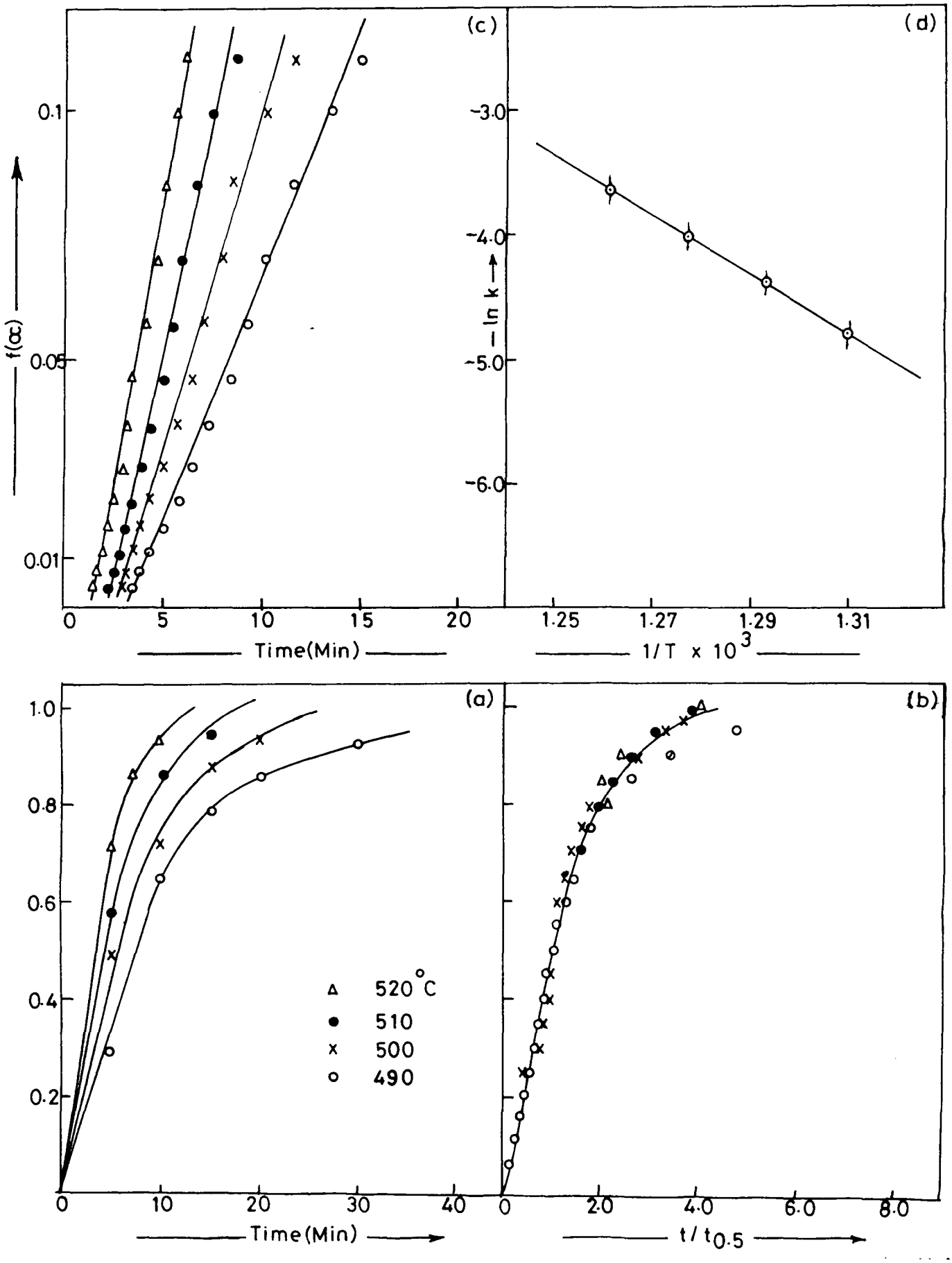

Fig. 4.15 : Isothermal TGA plots for γ -irradiated SrC_2O_4 + CuO (10%) (dose = 7.6 KGy)

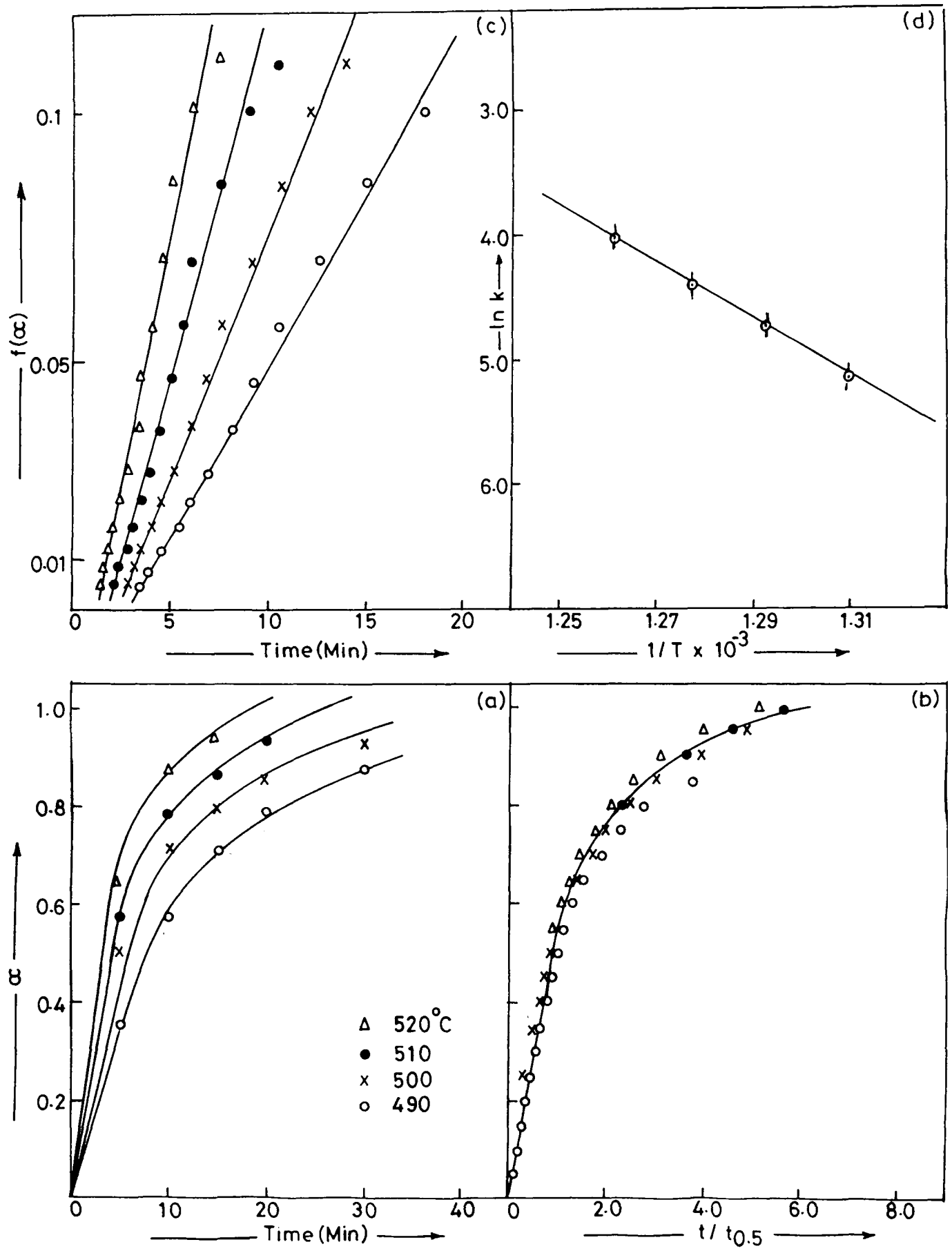

Fig. 4.16 : Isothermal TGA plots for γ -irradiated SrC_2O_4 + CuO (10%) (dose = 13.3 KGy

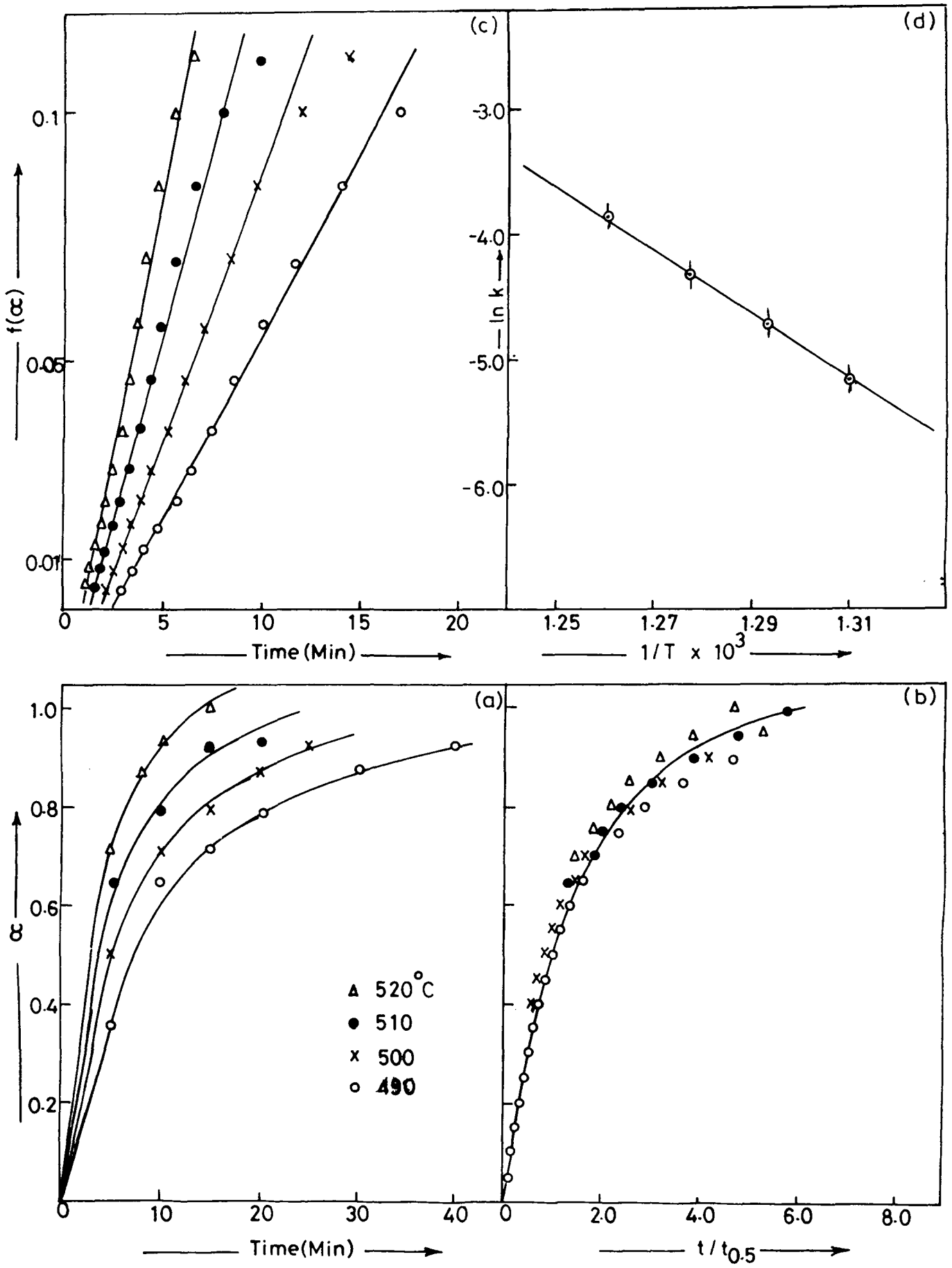

Fig. 4.17 : Isothermal TGA plots for γ -irradiated SrC_2O_4 + CuO (10%) (dose = 19.0 KGy).

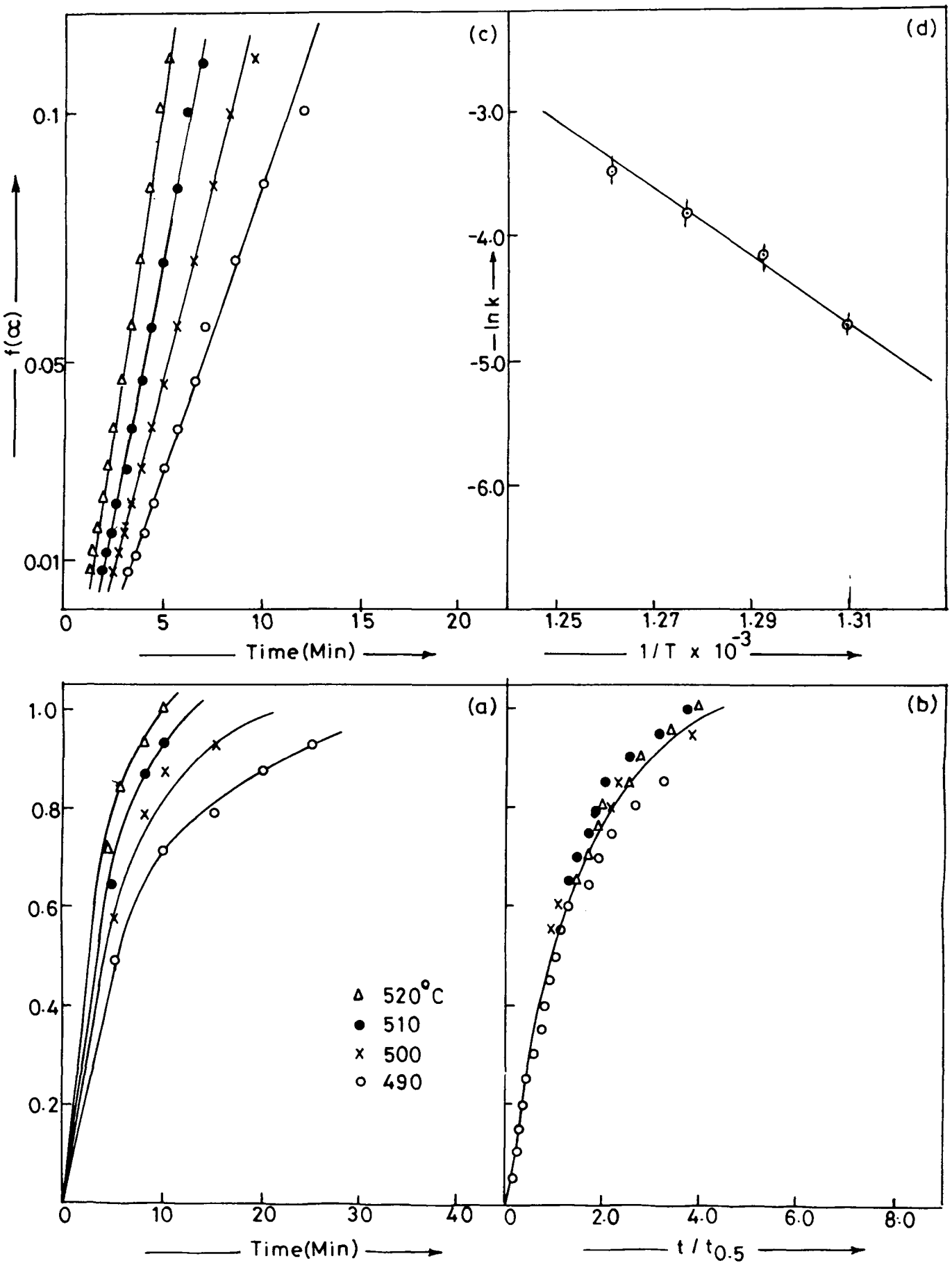

Fig. 4.18 : Isothermal TGA plots for γ -irradiated SrC_2O_4 + CuO (10%) (dose = 38.0 KGy).

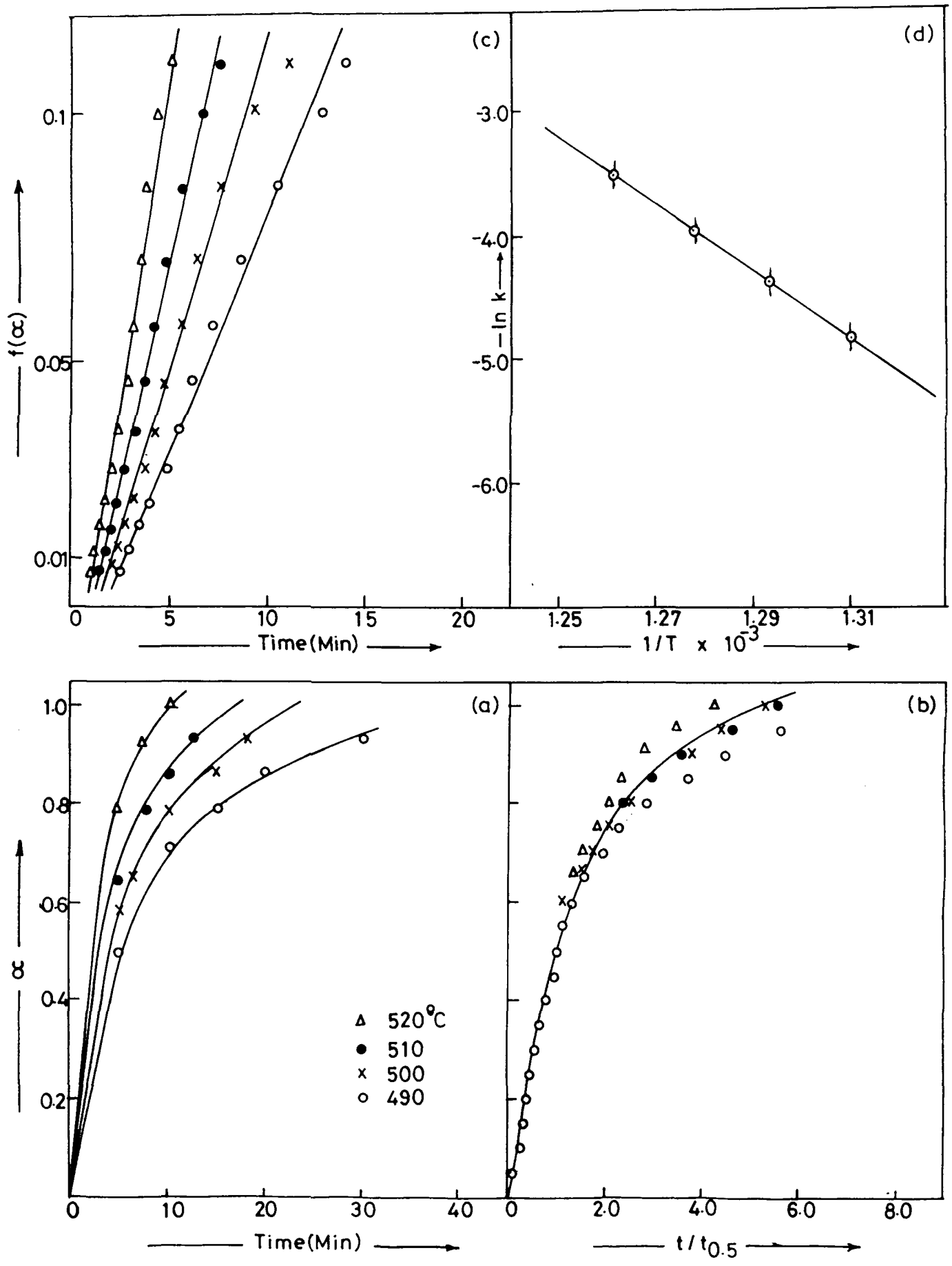

Fig. 4.19 : Isothermal TGA plots for γ -irradiated SrC_2O_4 + CuO (10%) (dose = 182 KGy).

Table 4.5 : Kinetic data of isothermal TGA of irradiated strontium oxalate + 10% ZnO additive samples.

Corrected irradiation dose absorbed (KGY)	Isothermal temperature ($T^{\circ}C$)	$1/T^{\circ}K$ X 10^{-3}	Rate constant K X10^{-3} (min^{-1})	lnk	Intercept X 10^{-2}	Ea. (kJ/mol)	ln A
0.0	490	1.310	2.94	- 5.83	- 0.75	238.0 ± 3	40.96
	500	1.293	5.97	- 5.12	- 1.19		
	510	1.277	11.36	- 4.48	- 2.82		
	520	1.261	23.47	- 3.75	- 3.19		
	530	1.245	47.29	- 3.65	- 4.23		
1.9	490	1.310	4.93	-5.31	-0.95	186.0 ± 2	30.56
	500	1.293	7.78	-4.84	-1.58		
	510	1.277	11.66	-4.45	-2.28		
	520	1.261	18.13	-4.01	-3.00		
	530	1.245	26.90	-3.43	-3.43		
7.6	490	1.310	5.17	-5.26	-0.75	145.0 ± 2	23.92
	500	1.293	7.86	-4.84	-0.88		
	510	1.277	13.25	-4.32	-1.34		
	520	1.261	22.27	-3.80	-1.87		
	530	1.245	33.33	-3.40	-		
13.3	490	1.310	6.7	-5.00	-1.29	88.0 ± 1	12.56
	500	1.293	10.1	-4.59	-1.40		
	510	1.277	14.2	-4.25	-1.89		
	520	1.261	20.0	-3.79	-2.28		
	530	1.245	34.21	-3.42	-2.63		
19.0	490	1.310	6.49	-5.037	-0.74	83.0 ± 1	11.92
	500	1.293	10.54	-4.55	-1.44		
	510	1.277	15.10	4.19-	-1.93		
	520	1.261	22.67	3.78-	-2.21		
	530	1.245	40.35	3.21-	-2.67		
38.0	490	1.310	12.72	4.36-	-2.38	89.0 ± 1	12.06
	500	1.293	18.72	3.99-	-2.75		
	510	1.277	23.85	3.73-	-2.83		
	520	1.261	30.00	3.50-	-2.90		
	530	1.245	45.00	3.10-	-3.05		
182.0	490	1.310	11.76	-4.42	-2.06	78.0 ± 1	11.73
	500	1.293	17.55	-4.04	-2.10		
	510	1.277	22.63	-3.78	-1.63		
	520	1.261	33.40	-3.39	-1.73		
	530	1.245	46.84	-3.061	-1.69		

Table 4.6 : Kinetic data of isothermal TGA of irradiated strontium oxalate + 10% CuO additive samples

Corrected irradiation dose absorbed (KGY)	Isothermal temperature ($T^{\circ}C$)	$1/T^{\circ}K \times 10^{-3}$	Rate constant $K \times 10^{-3}$ (min^{-1})	Ink	Intercept $\times 10^{-2}$	Ea. (kJ/mol)	In A
0.0	490	1.310	4.58	- 5.38	- 0.87	128 ± 1	22.98
	500	1.293	7.75	- 4.86	- 1.51		
	510	1.277	10.25	- 4.58	- 1.25		
	520	1.261	16.50	- 4.10	- 2.21		
1.9	490	1.310	5.53	-5.19	-0.85	224 ± 2	37.59
	500	1.293	8.20	-4.80	-1.28		
	510	1.277	12.45	-4.37	-1.43		
	520	1.261	21.65	-3.83	-2.39		
7.6	490	1.310	8.37	-4.78	-1.94	176 ± 2	30.05
	500	1.293	12.53	-4.38	-2.58		
	510	1.277	17.90	-4.02	-3.18		
	520	1.261	24.57	-3.70	-3.17		
13.3	490	1.310	6.05	-5.10	-1.04	188 ± 2	31.66
	500	1.293	8.75	-4.73	-1.21		
	510	1.277	12.28	-4.39	-1.47		
	520	1.261	18.50	-4.01	-1.64		
19.0	490	1.310	5.82	-5.14	-0.68	217 ± 2	36.43
	500	1.293	8.55	-4.76	-0.72		
	510	1.277	12.92	-4.35	-1.05		
	520	1.261	21.59	-3.83	-1.86		
38.0	490	1.310	9.10	-4.69	-1.23	191 ± 2	32.69
	500	1.293	16.24	-4.11	-2.65		
	510	1.277	22.53	-3.79	-2.92		
	520	1.261	29.30	-3.53	-2.81		
182.0	490	1.310	8.00	-4.827	-0.67	211 ± 2	35.77
	500	1.293	12.78	-4.36	-1.500		
	510	1.277	18.13	-4.00	-1.45		
	520	1.261	29.64	-3.52	-2.37		

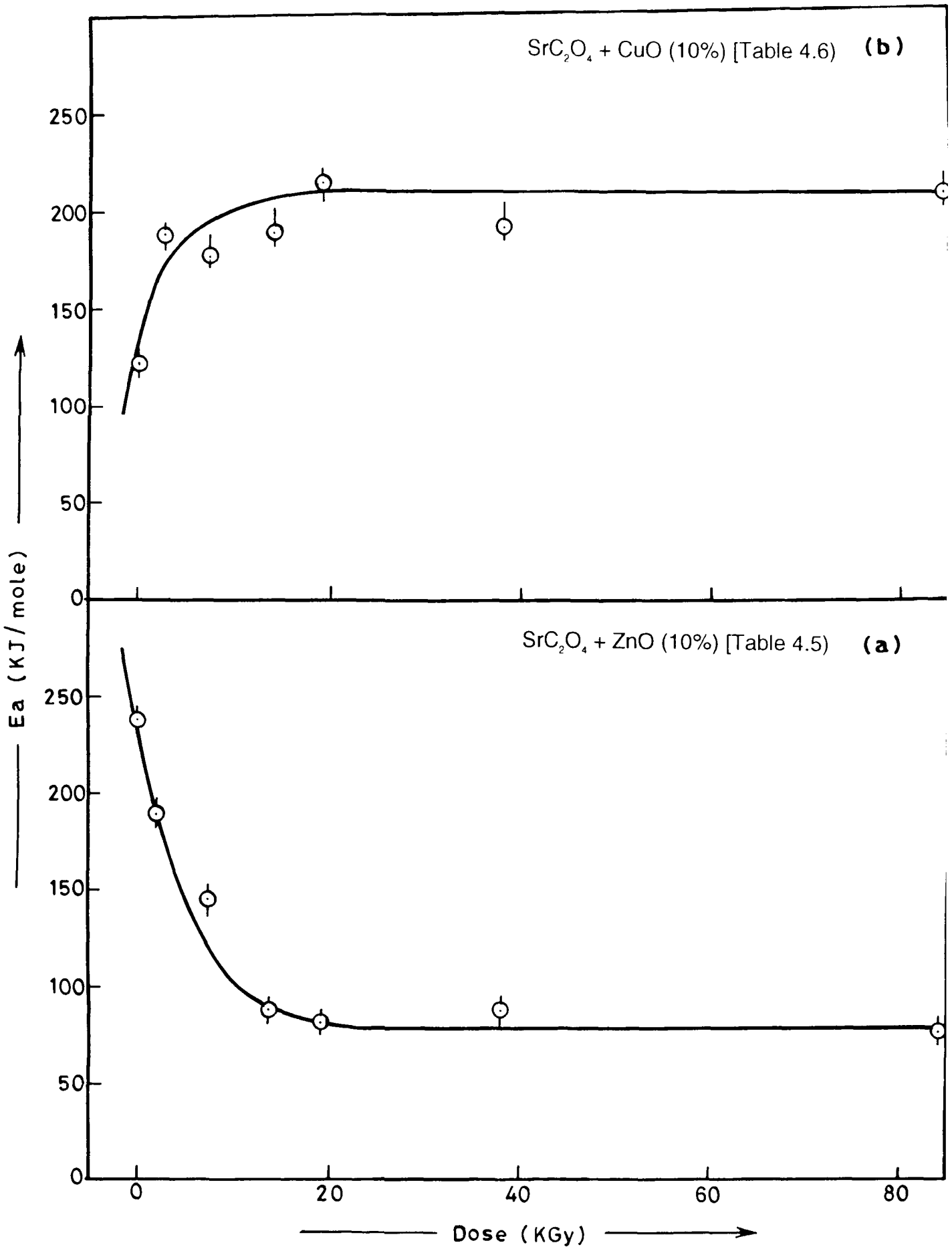

Fig. 4.20 : Plots of energy of activation versus absorbed dose for both γ - irradiated (a) SrC_2O_4 + ZnO and (b) SrC_2O_4 + CuO from isothermal TGA.

dose when zinc oxide is used as an additive. An exponential increase in the energy of activation with dose is observed in case of strontium oxalate with copper oxide additive.

4.3 DISCUSSION

The physical incorporation of metal oxide and salts[194,195] and also irradiation[196-199] are known to influence the thermal decomposition characteristics of many inorganic solids. In the present investigation a noticeable effect on decomposition temperature and energy of activation is observed by incorporating the zinc and copper oxides in strontium oxalate (Table 4.1). In the case of dynamic TGA of unirradiated binary mixtures, the presence of copper oxide showed enhanced effect on both decomposition temperature and energy of activation than zinc oxide. However, irradiation of binary mixture of oxalate containing zinc oxide showed a pronounced decreasing trend than for oxalate containing copper oxide additive (Tables 4.2 and 4.3).

The non-stoichiometric solids play an important role in catalysis of solid state thermal decomposition reactions[200-202]. In many such reactions the diffusion of reactant or product is rate controlling and diffusion is possible only because of lattice defects of various types. Another important factor is the lattice strain arising due to impurity atoms of such a nature as to disturb the regularity of the lattice. This strain acts as a source of energy and it may increase the ease with which imperfections form and hence increase the rate of thermal decomposition reactions.

The oxide effect is explained on the basis of the type of oxide used for the decomposition of oxalate. The oxides are classified into n- and p-ype of semiconductors. Zinc oxide is known as an n-type semiconductor[203,204]. Its behaviour at high temperature is very important in thermal decomposition reactions. At higher temperature zinc oxide loses neutral oxygen so that zinc is in excess. This zinc atom accepts two electrons from the oxalate ion in a binary mixture. It facilitates

the breaking of a C-O bond. Hence the rate of thermal decomposition increases in the presence of an n-type semiconductor like zinc oxide.

Copper oxide is a p-type semiconductor[204,205], in which cationic sites are vacant with positive holes existing at the oxygen atoms. On heating there is loss of positive ion from lattice. Hence to preserve electrical neutrality, electrons from the oxalate are accepted. This process is predominant in the presence of copper oxide in binary mixture resulting in the breaking of an oxalate bond. Thus, the enhanced decomposition rate of oxalate in the presence of copper oxide as compared to zinc oxide can be explained on the basis of n- and p-type of semiconductor behaviour. Both the oxides act as catalysts. The extent of catalytic decomposition is dependent on the type of oxide. It is well known that p-type oxides are the better catalysts than n-type oxides[206,207]. The results obtained in the present investigation are in accordance with the above statement.

4.3.1 Irradiation Effect on Binary Mixture

Radiation has been seen to produce in solids and consequently at their surface, both structural imperfections and excited states. It modify the Fermi level position in solids and hence its catalytic activity. It is well known that the catalytic irradiation in presence of reactants can modify to a considerable extent the kinetics of the catalytic reaction.[208]

It is observed that the kinetic parameters are considerably changed when thermal decomposition of strontium oxalate with oxide additives was studied after γ - irradiation. This is mainly due to lattice defects, trapped charges and reduced products formed in crystal lattice because of gamma irradiation. After γ - irradiation of strontium oxalate and oxide admixture the thermal decomposition study is carried out. The thermal decomposition of strontium oxalates with zinc oxide additive on irradiation showed an enhanced effect than copper oxide additive. This is explained on the basis of structural modification of semi conducting oxides on γ - irradiation.

It is well known that acceptor (n - type) reactions are catalysed by electrons while donar (p - type) reactions are catalysed by positive holes[209]. Vesselovsky **[210]** proposed that the multiplication of number of minority carriers takes place to many times in either type of semiconductors after irradiation. The multiplication factor **[210]** for minority carriers which are positive holes in case of ZnO on irradiation is 4×10^5. In certain cases because of irradiation the stationary concentration of these minority carriers get multiplied by several powers of ten **[211 - 212]**. Lark. Horo witz.et.al.**[213]** predicted that a large number of positive holes are created on irradiation of a n-type semiconductor. This reduces the conductivity resulting in the formation of a intrinsic semiconductor. Which upon further irradiation shows increase in conductivity; but it becomes a p - type Semiconductor. A remarkable structures modification in the semiconductors appears when the lattice defects are created by radiation.**[214]**

The number of positive holes created in zinc oxide after irradiation enhances its catalytic activity. On the other hand there is no much change in the activity of CuO on irradiation. The catalytic activity of ZnO enhances on irradiation resulting in a sharp decrease in the energy of activation for the thermal decomposition of strontium oxalate. In other words, the zinc oxide becomes more efficient catalyst than copper oxide on irradiation for thermal decomposition of strontium oxalate.

Irradiation promotes the rate of thermal decomposition of strontium oxalate to a greater extent in the presence of zinc oxide and copper oxide. It is of interest to find out whether there is any compensation effect present on irradiation of binary mixtures as observed in Chapter III for thermal decomposition of irradiated strontium oxalate.

A graph of lnA versus Ea is plotted from the dynamic TGA data of irradiated binary mixture of oxalate and zinc oxide. This graph is shown in Fig. 4.21. Similarly a plot of lnA versus Ea for isothermal TGA of irradiated binary mixture is shown in Fig. 4.22. The plots of lnk versus 1/T

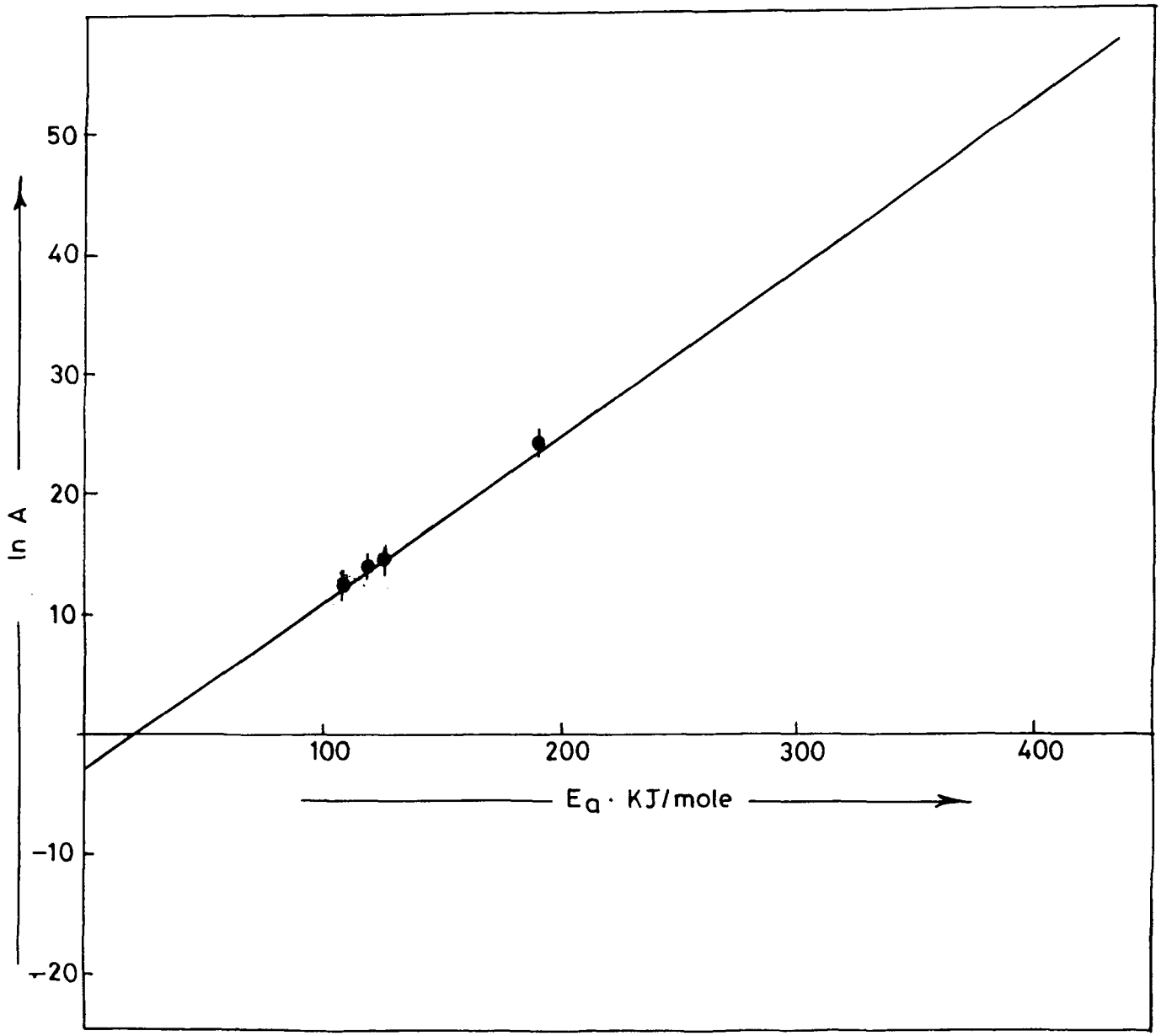

Fig. 4.21 : Kinetic compensation effect from dynamic TGA of γ - irradiated SrC_2O_4 + ZnO (10%).

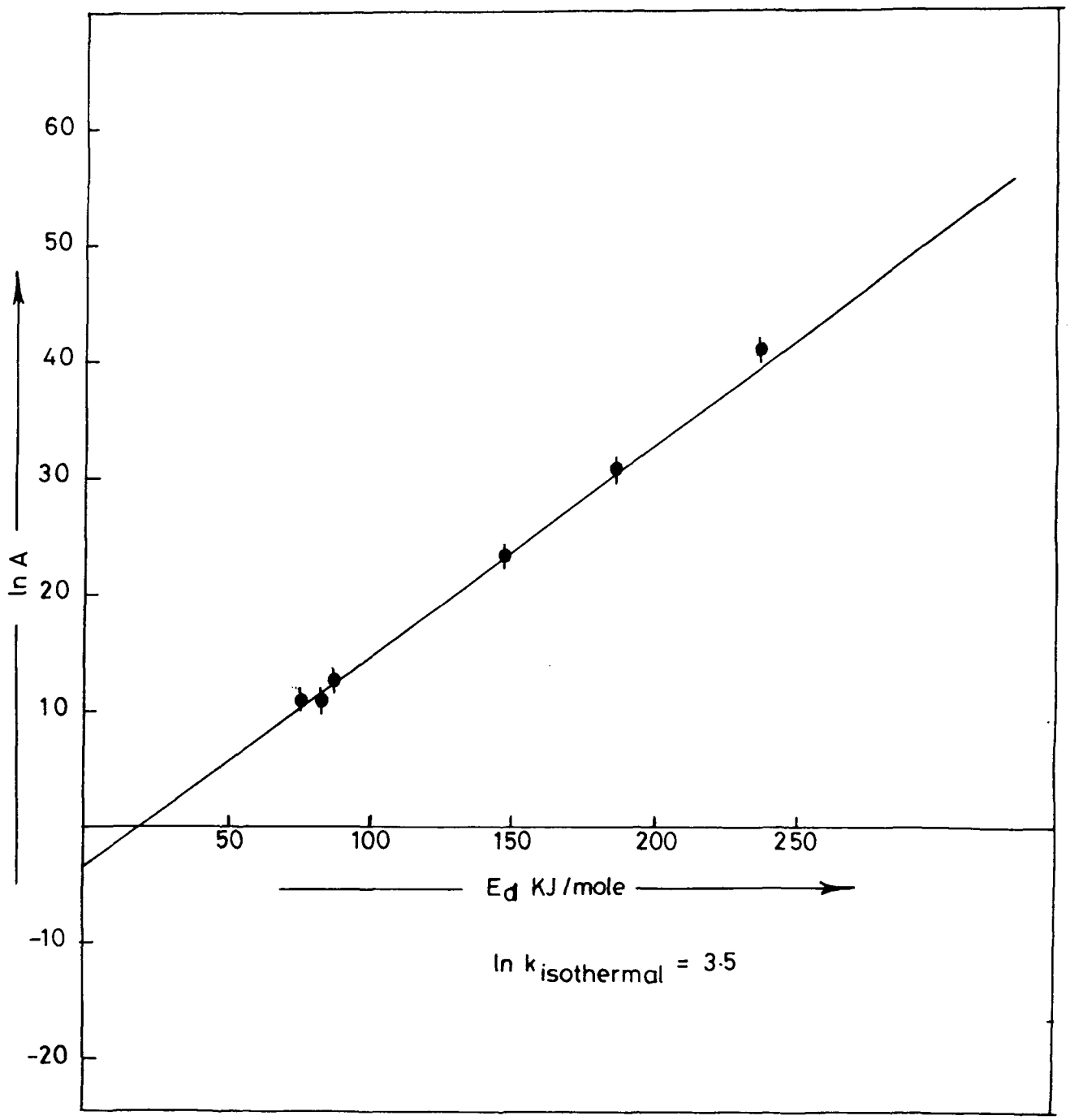

Fig. 4.22 : Kinetic compensation effect from isothermal TGA of γ - irradiated SrC_2O_4 + ZnO (10%).

obtained from isothermal TGA of binary mixture of oxalate and zinc oxide irradiated for various doses are shown in Fig. 4.23. It is observed from the above figures that

(1) The lnA versus Ea plot is linear with positive slope and intercept equal to lnk.

(2) There is an isokinetic point in the plots of lnk versus 1/T which gives values of isokinetic temperature T_{iso} and isokinetic rate constant k_{iso}.

(3) The experimental data lies on both sides of the isokinetic point.

These observations are summarised in Table 4.7. Since all the three conditions of kinetic compensation effect are satisfied in case of binary mixture of oxalate and zinc oxide, one can confirm the kinetic compensation effect as a result of irradiation of the above binary mixture.

A similar procedure is followed to find out the kinetic compensation effect in binary mixture of irradiated strontium oxalate containing copper oxide additive.

(1) The plot of lnA versus Ea for dynamic and isothermal TGA of binary mixture are shown in Figs. 4.24 and 4.25 respectively. these plots are linear having an intercept equal to zero. Therefore lnk is zero and hence k = 1.

(2) The plots of lnk versus 1/T, for irradiated binary mixture of oxalate and copper oxide are shown in Fig. 4.26. All these plots are linear and parallel to each other. There is no possibility of the existence of an isokinetic point.

(3) Since there is no isokinetic point the third condition is not obeyed.

From the above observations, it is clear that the kinetic compensation effect is totally absent in the case of irradiated oxalate containing copper oxide.

It is interesting to note that whenevr there is a sharp decrease in the energy of activation on irradiation of pure substance or binary mixture of two substances a kinetic compensation effect is observed. The decrease in energy of activation results in decreasing the pre-exponential factor in the Arrhenius equation. If there is no sharp decrease in the energy of activation then the pre-

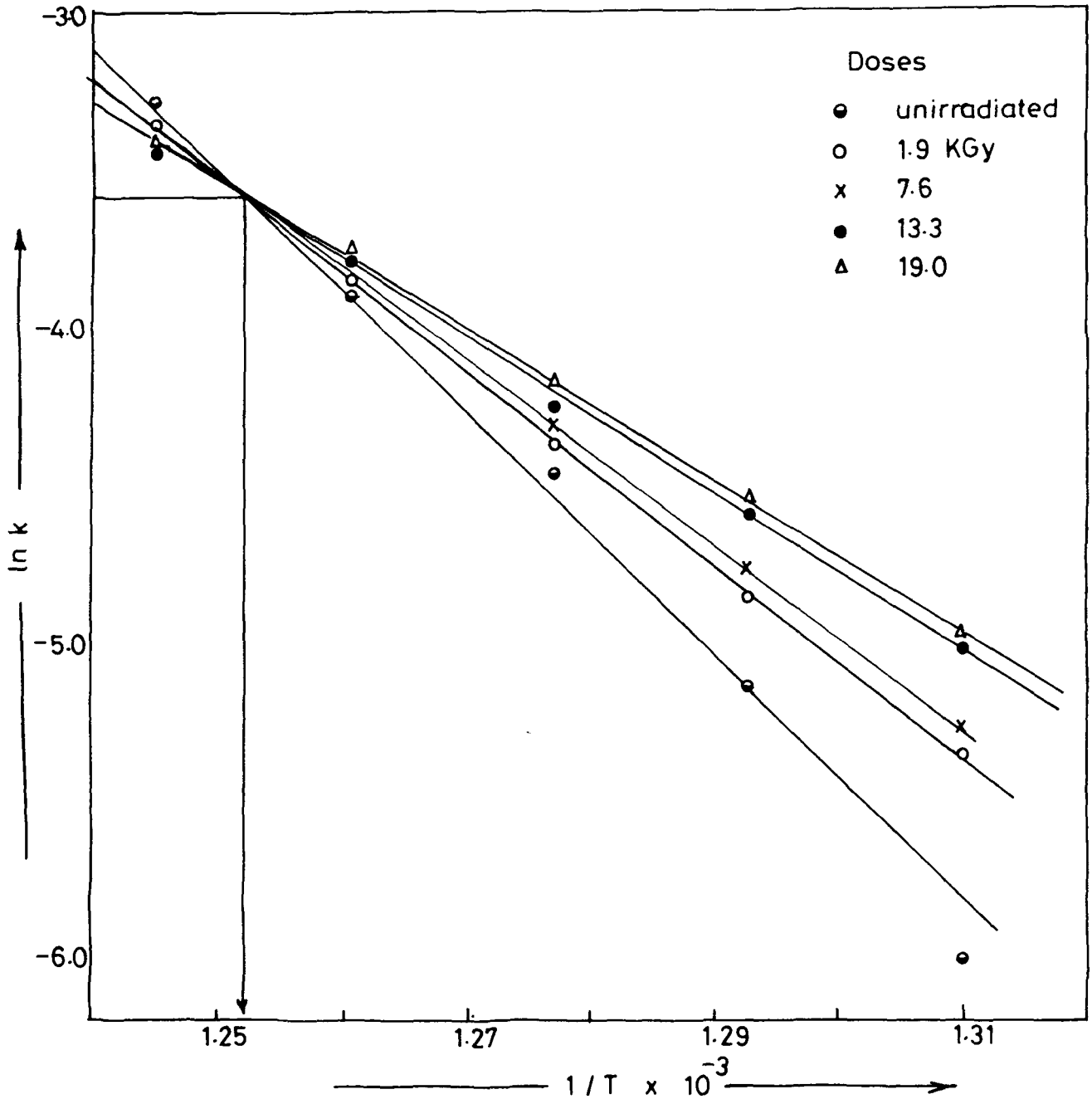

Fig. 4.23 : Compensation effect from isothermal TGA of γ - irradiated SrC_2O_4 + ZnO (10%).

Table 4.7 : Kinetic compensation parameters of irradiated SrC_2Or_4 +10% ZnO samples.

Parameter	From dynamic TGA plot of ln A vs Ea	From isothermal TGA	
		Plot of ln A vs Ea	Plot of lnk vs 1/T
lnk_{iso}	-3.30	-3.5	-3.6
$1/T_{iso}$	1.245 X 10-3	1.253 X 10-3	1.252 X 10-3
T_{iso}	803.21	798.08	800.00
K_{iso}	0.036	0.030	0.027

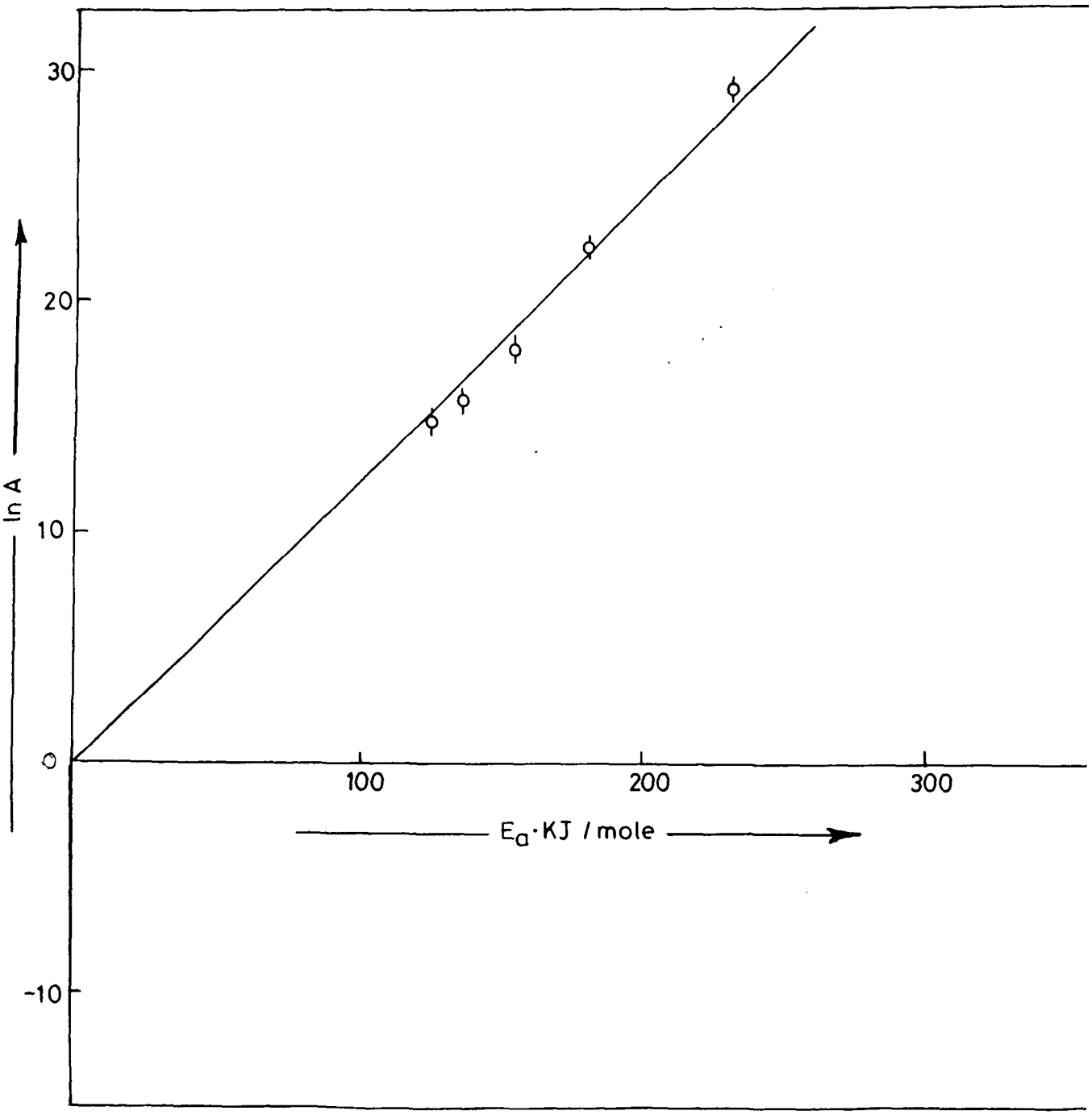

Fig. 4.24 : Plots of ln A vs Ea for γ - irradiated SrC_2O_4 + CuO (10%) from dynamic TGA

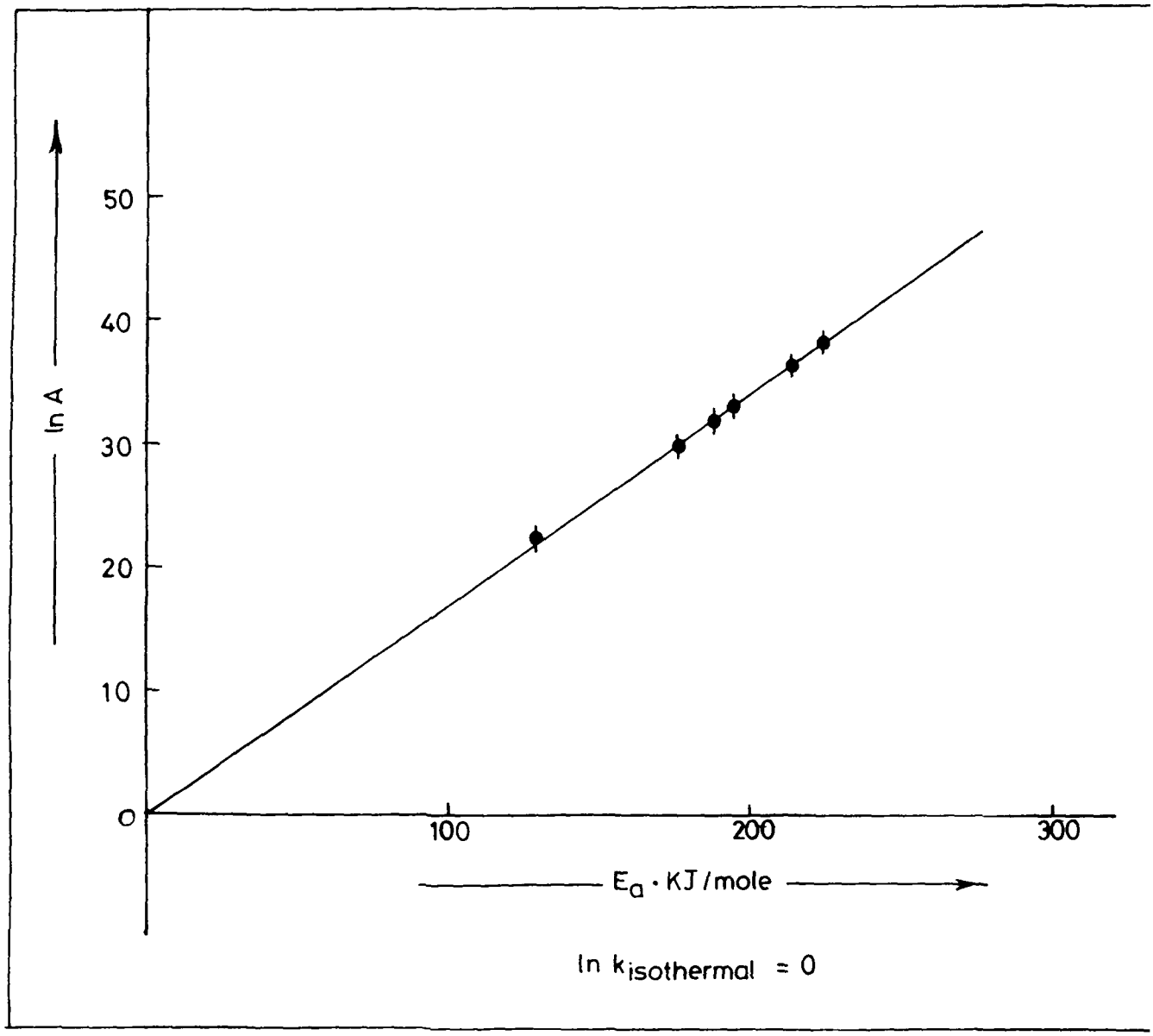

Fig. 4.25 : Plots of ln A vs Ea for γ -irradiated SrC_2O_4 + CuO (10%) from isothermal TG

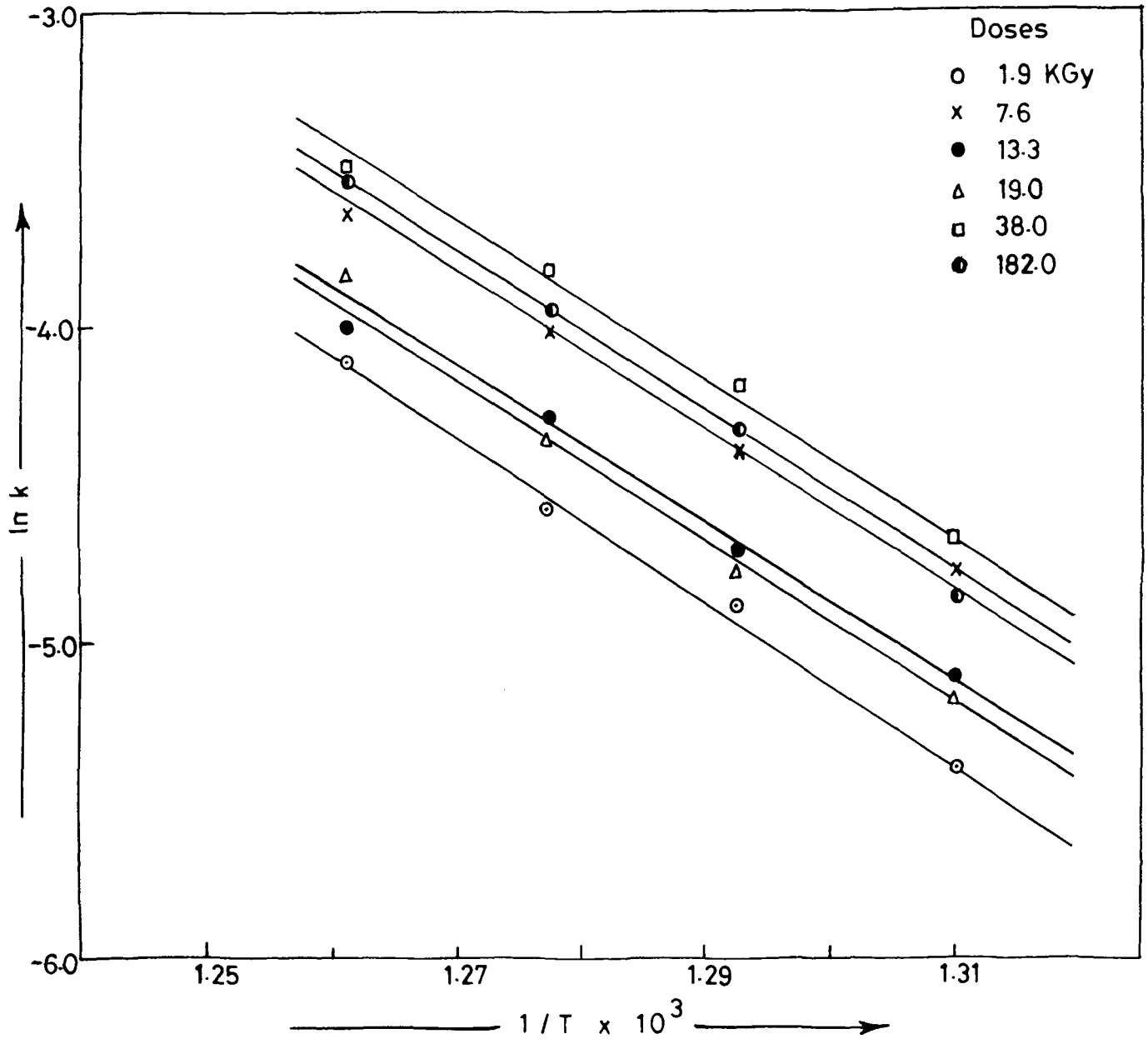

Fig. 4.26 : Plots of lnk vs 1/T from isothermal TGA of irradiated SrC_2O_4 + CuO (10%).

exponential factor in the Arrhenius equation does not change. In such systems the kinetic compensation effect will not be observed. For example the binary mixtures of oxalate and copper oxide on irradiation do not show large and sharp changes in the energy of activation; hence the pre-exponential factor in the Arrhenius equation does not change. Experimentally there is no kinetic compensation effect observed in the above system. On the other hand, the energy of activation for irradiated pure strontium oxalate and binary mixtures of oxalate and zinc oxide show a sharp decrease. This results in decreasing the pre-exponential factor in Arrhenius equation. The true kinetic compensation effect is experimentally noticed in the latter system.