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Thermochimica Acta 383 (2002) 95–101

thermochimica acta

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Kinetics of the thermal decomposition of γ-irradiated gadolinium acetate

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Received 23 May 2001; accepted 28 June 2001

Abstract

Kinetics of the thermal decomposition of un-irradiated (pristine) and pre-γ-irradiated hydrated gadolinium acetate was studied within the temperature range (603–623 K) and in air using isothermal and dynamics thermogravimetric techniques. The data were analyzed using various solid-state reaction models. Integral method using Coat–Redfon equation was applied in dynamic data analysis. The results showed that the kinetic of isothermal and non-isothermal (dynamic) decomposition for acceleratory stage was governed by phase boundary process. The activation energies for pristine and pre-irradiated samples were calculated and the results of the isothermal and dynamic decomposition integral methods were compared and discussed. Thermodynamic values of the main decomposition process were calculated and evaluated.

Keywords: Gadolinium acetate; Isothermal and non-isothermal decomposition; γ-Irradiated

1. Introduction

Thermal decomposition of solids is an important field of solid-state chemistry with wide technical applications [1]. Pre exposure to ionizing radiation (γ-ray or UV light) was found to accelerate the isothermal decomposition of solids. However, details of the kinetics were not reported [2]. Previous work on the thermal decomposition of metal acetates indicated that the isothermal decomposition kinetics could be effected markedly by prior exposure to ionizing radiation [3–5]. In general, the effects with increasing dose are a shortening of the induction period followed by an overall decrease in time required to complete the reaction [6]. Metal acetates represent an important class of the compounds with wide technical and biological applications.

In the present investigation, the kinetics of the thermal decomposition of hydrated gadolinium acetate before and after γ-irradiation was studied by isothermal and dynamic thermogravimetry (TG).

2. Experimental

Hydrated gadolinium acetate was obtained commercially (WINLAB, England) and used without further purification.

The decomposition of gadolinium acetate in air yields Gd_2O_6 and some volatile products and within experimental error the process eventually goes to completion [7]. The investigated sample weights were in the range of 100 mg. The decomposition was followed in air using isothermal and dynamic thermogravimetric

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PII: S0040-6031(01)00682-7

techniques in the temperature range (603–623 K) using Netzsch STA 429, thermal analyzer (Germany). For isothermal measurement the heating rate was (5 °C/min). Under non-isothermal conditions three different heating rates 5, 10, and 20 °C/min were applied.

For irradiation, samples were encapsulated under vacuum in glass vials and were exposed to successively increasing doses of radiation at constant intensity using Co-60 γ-ray cell 220 (Nordion INT-INC, Ontario, Canada) at a dose rate of 10^4 Gy/h. The source was calibrated against fricke ferrous sulphate dosimeter and the dose rate in the irradiated samples was calculated by applying appropriate corrections on the basis of photon mass attenuation and energy-absorption coefficient for the sample and the dosimeter solution [8].

3. Results and discussion

3.1. Isothermal decomposition

Fig. 1 shows TG and differential thermogravimetry (DTG) curves of the thermal decomposition of hydrated gadolinium acetate in air. The TG curve shows that the decomposition of $Gd(CH_3COO)_3$ takes place in three steps. The dehydration step commences at ≈393 K corresponds to loss of ≈$3H_2O$ molecules. The weight loss was estimated to about 17.4% of the total weight in good agreement with the theoretical calculated value (16.4%). The decomposition of dehydrated $Gd(CH_3COO)_3$ proceeds in two steps the first step in the temperature range (583–863 K) corresponding to formation of $Gd_2O_2CO_3$ and volatile products. The second step in the temperature range (933–1013 K) corresponding to formation of Gd_2O_3 and CO_2. The experimentally calculated total weight loss value of the whole decomposition process is in good agreement with the theoretical calculated one [9]. Fig. 2 shows α–t curves of the isothermal decomposition of un-irradiated and pre-γ-irradiated gadolinium acetate (total dose 10^6 Gy) at three different decomposition temperatures (603, 613 and 623 K), where α is the fraction decomposed at decomposition time t. The curves show an increase in the fraction decomposed α with an increase in the decomposition time t up to a maximum value (α_{max}) depending on the temperature investigated. In general, the isothermal decomposition of both un-irradiated and pre-γ-irradiated material produces sigmoid α versus t curves in the range (603–623 K). Shortening of the induction period and acceleration in time required to reach α_{max} at a given temperature was observed markedly in the decomposition γ-irradiated sample of gadolinium acetate. This behavior could be attributed to the formation of additional nucleation sites. The additional nucleation centers enhance all of the decomposition stages (induction period, acceleratory region and decay stage).

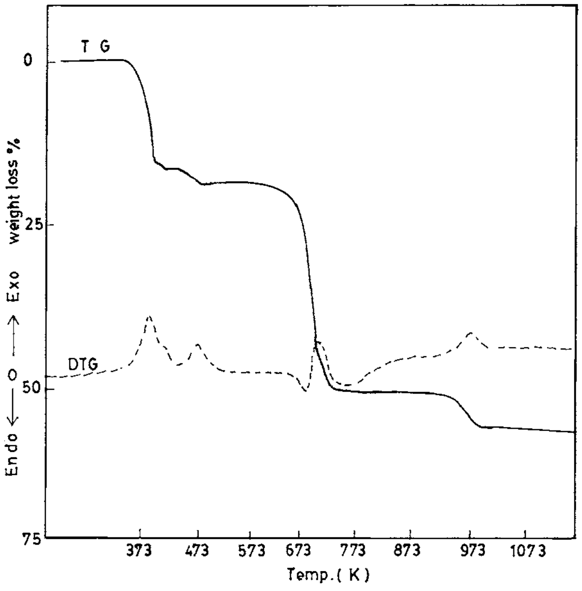


Fig. 1. TG and DTG of gadolinium acetate.

The isothermal α/t data for the main process, i.e. the acceleratory region of gadolinium acetate decomposition ($0.15 < \alpha < 0.956$) was analyzed according to the various kinetic mechanisms and cited in Table 1 [6]. Under isothermal conditions, the rate constant k, is independent of the reaction time and so $kt = g(\alpha)$. A plot of $g(\alpha)$ versus t should give a straight line if the correct form of $g(\alpha)$ versus t is reached. The function $g(\alpha)$ depends on the mechanism controlling the reaction, the size and shape of the reacting particles [10]. In a diffusion-controlled reaction: D is the function for a one-dimensional diffusion process governed by a parabolic law, with constant diffusion coefficient; D_2 is for a two-dimensional diffusion-controlled process into a cylinder; D_3 is Jander's equation for diffusion-controlled reaction in a sphere and D_4 is a function for a diffusion-controlled reaction starting on the exterior

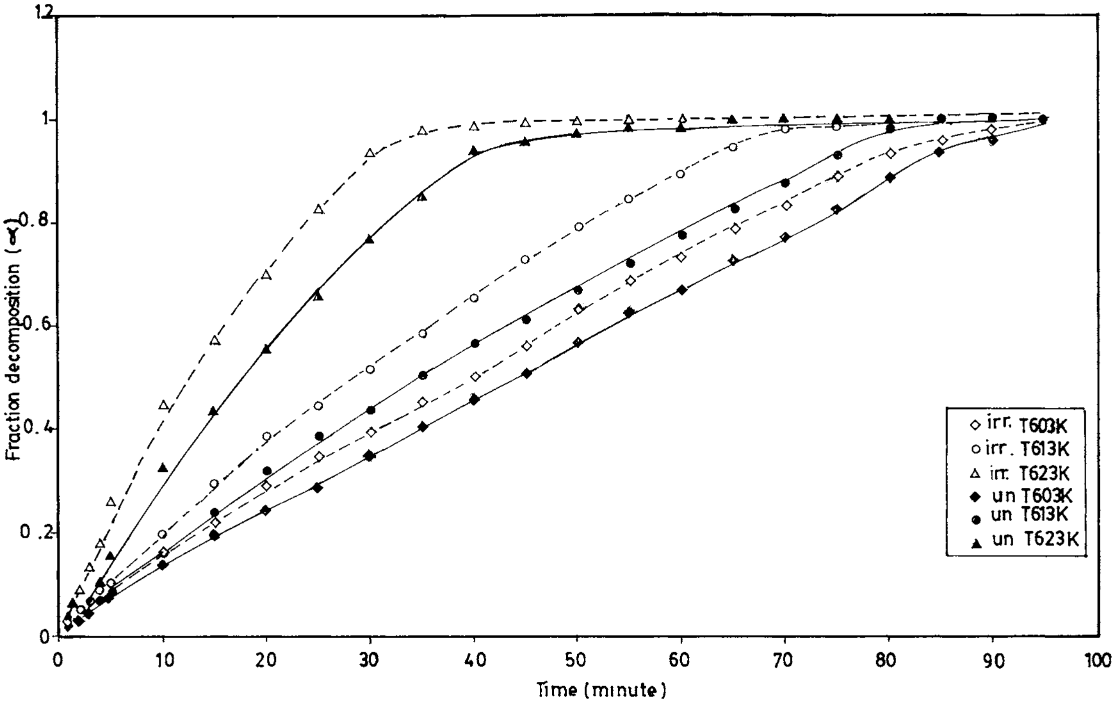


Fig. 2. Fractional decomposition α vs. time curves for the isothermal decomposition of gadolinium acetate.

of a spherical particle. In phase–boundary-controlled reactions, the reaction is controlled by movement of an interface at constant velocity and nucleation occurs virtually instantaneously, then, the equation relating α and t is the R_2 function for a circular disc reacting from the edge inward and the function R_3 for a sphere reacting from the surface inward. If the solid-state reaction follows first-order kinetic (F_1 function) then the rate-determining step is the nucleation process and there is an equal probability of nucleation at each active site. In phase–boundary reaction, it is assumed that the nucleation step occurs instantaneously, so that the surface of each particle is covered with a layer of the product. Nucleation of the reactant, however, may be a random process, not followed by rapid surface growth. As the nuclei grow larger, they must eventually impinge on one another, so that growth ceases where they touch. This process has been considered by Avrami and Erofe'ev, who have given the functions A_2 and A_3, respectively [11]. Our results show that

Table 1
Mechanistic equation examined in this work

Equation	Function	Function
One-dimensional diffusion	α^2	D_1
Two-dimensional diffusion	$(1-\alpha)\ln(1-\alpha)+\alpha$	D_2
Jander equation, three-dimensional diffusion	$[1-(1-\alpha)^{1/3}]^2$	D_3
Ginstling–Brounshtein equation three-dimensional diffusion	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	D_4
Two-dimensional phase–boundary reaction	$1-(1-\alpha)^{1/2}$	R_2
Three-dimensional phase–boundary reaction	$1-(1-\alpha)^{1/3}$	R_3
First-order kinetic	$\ln(1-\alpha)$	F_1
Random nucleation: Avrami equation	$-[\ln(1-\alpha)]^{1/2}$	A_2
Random nucleation: Erofe'ev equation	$-[\ln(1-\alpha)]^{1/3}$	A_3

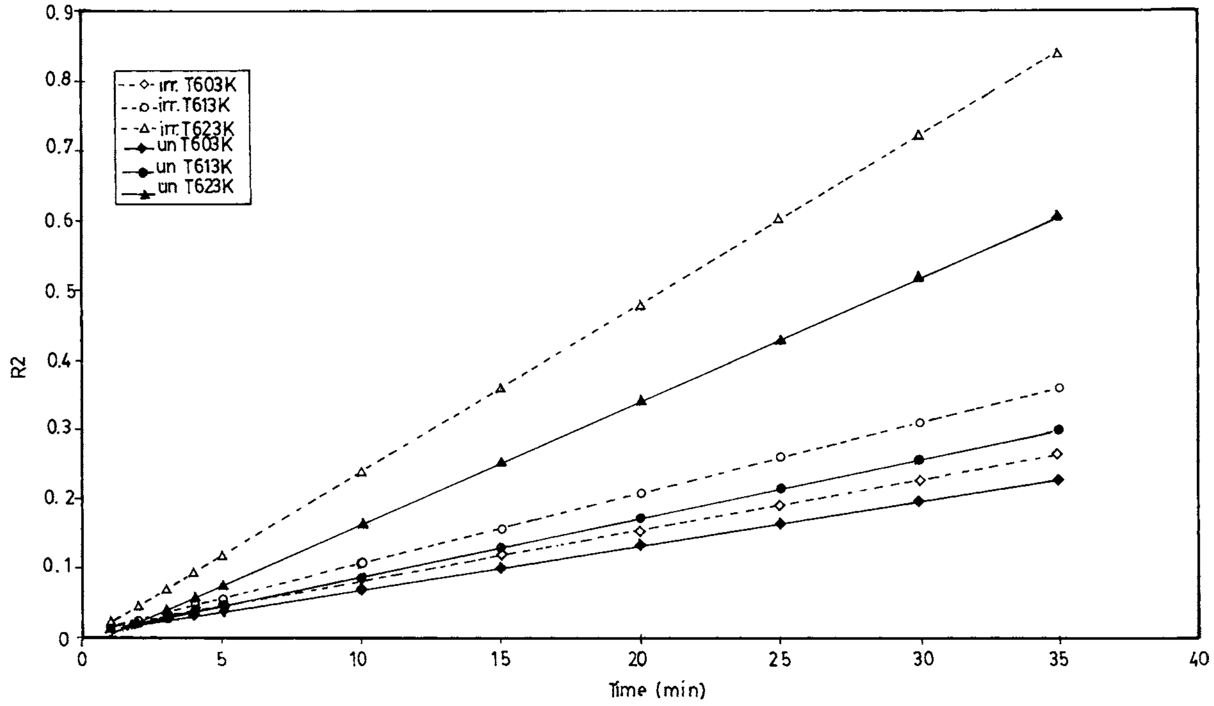


Fig. 3. Isothermal decomposition reaction for gadolinium acetate according to two-dimensional diffusion.

isothermal data of gadolinium acetate samples obey two-dimensional phase–boundary reaction (R_2) models (Fig. 3). Kinetic energy of the main decomposition processes, i.e. the acceleratory region for pristine and pre-irradiated material was calculated by applying the least square method (lsm) using Arrhenius equation. The results are tabulated in Table 2.

3.2. Non-isothermal decomposition

Non-isothermal decomposition of un-irradiated and pre-γ-irradiated gadolinium acetate sample is shown in (Fig. 4). The rate is set to a constant value β and the function $g(\alpha)$ is given by Doyle's equation [12]

$$g(\alpha) = \left(\frac{A}{B}\right)\int_0^T \exp\left(\frac{-E}{RT}\right)\,\mathrm{d}t = \frac{AE}{R\beta}p(x).$$

The fraction $p(x)$ has been defined as

$$p(x) = \frac{\mathrm{e}^{-x}}{x} - \int_x^\infty \frac{\mathrm{e}^{-\mu}\,\mathrm{d}\mu}{\mu}$$

where $\mu = E/RT$ and x is the corresponding value of μ at which a fraction α of material has decomposed. In the Coats–Redfon method, the function $g(\alpha)$ is

Table 2
Kinetic parameters of the isothermal and non-isothermal decomposition of gadolinium acetate

Kinetic parameters	Isothermal technique	(Non-isothermal technique)[a]		
		(5)	(10)	(20)
E_a (kJ mol^{-1}) un-irradiated	160.12	149.79	152.99	121.24
γ-Irradiated (10^6 Gy)	188.48	148.59	144.99	138.48
ln A (min^{-1}) un-irradiated	26.12	–	–	–
γ-Irradiated (10^6 Gy)	32.56	–	–	–

[a] Heating rate (°C/min).

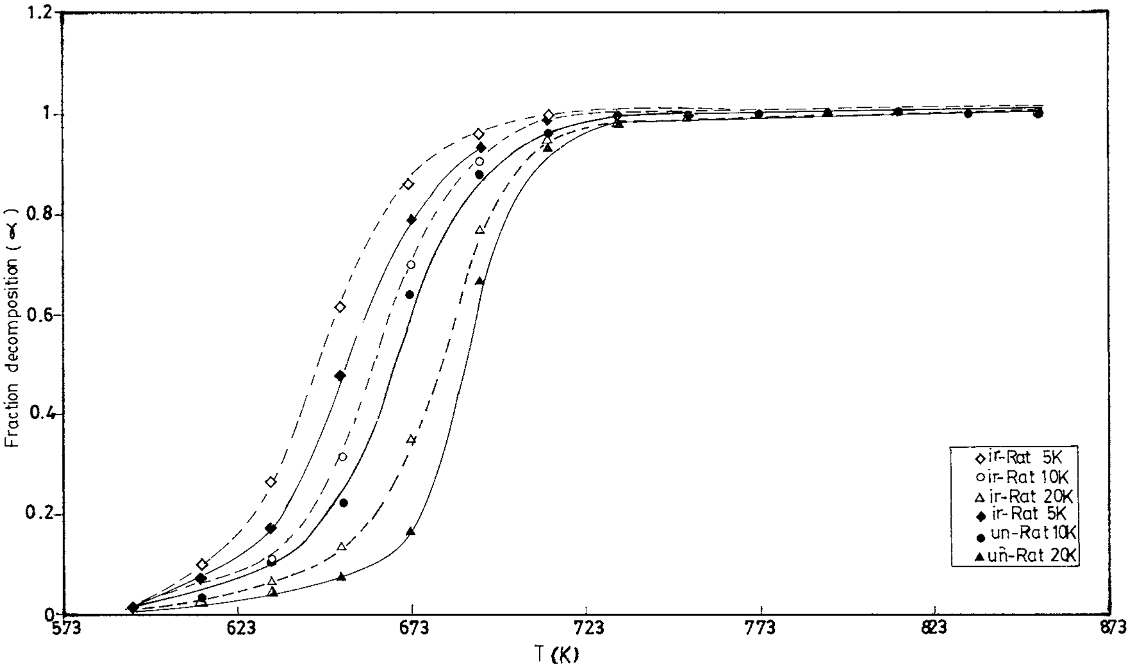


Fig. 4. Dynamic measurements for gadolinium acetate thermal decomposition.

approximated to the form

$$\log\frac{g(\alpha)}{T^2} = \log\frac{AR}{E\beta} - \frac{E}{2.3RT}.$$

Accordingly, $\log(g(\alpha)/T^2)$ is to be calculated and plotted against $1/T$ for all possible mechanisms and the best straight line determines the operating mechanism. The values of E_a and A are calculated from the slope and intercept [13]. Fig. 5 shows the results of data analysis performed according to Coats–Redfon equation. The results indicate that the best fit of dynamic data of gadolinium acetate was achieved using two-dimensional phase–boundary reaction (R_2) models. The calculated kinetic parameters using dynamic isothermal techniques are tabulated in Table 2. It should be mentioned that in non-isothermal (dynamic) technique, the calculated E_a values for γ-irradiated salt show relatively higher compared with the values calculated for un-irradiated (pristine) salt. This difference in activation energy values was significantly observed in the isothermal measurements. Creation of trapped holes, electron and radicals in the host lattice of γ-irradiated gadolinium acetate retard the decomposition process and reduce the number of reactive sites available for the decomposition.

Entropy and enthalpy values of he main decomposition process were calculated using the following equation [14]:

$$\ln\frac{k}{T} = \frac{-\Delta H^{\#0}}{RT} + \ln\frac{R}{Nh} + \frac{\Delta S^{\#0}}{R}$$

where k is the rate constant, R the gas constant, T the absolute temperature, N Avogdro's number and h is the Plank constant. Plotting $\ln k/T$ against $1/T$, the slope and intercept give $\Delta H^{\#0}$ and $\Delta S^{\#0}$, respectively. The calculated values are included in Table 3.

4. Role of irradiation

Upon irradiation with ^{60}Co γ-ray, the Compton effect has the largest cross-section in very light elements and diminishes to zero around atomic number 125 [15]. The possibility of displacement of gadolinium (atomic weight 157.3) by Compton electrons is very low. Generation of additional sites of potential nucleation are produced by γ-ray. These may

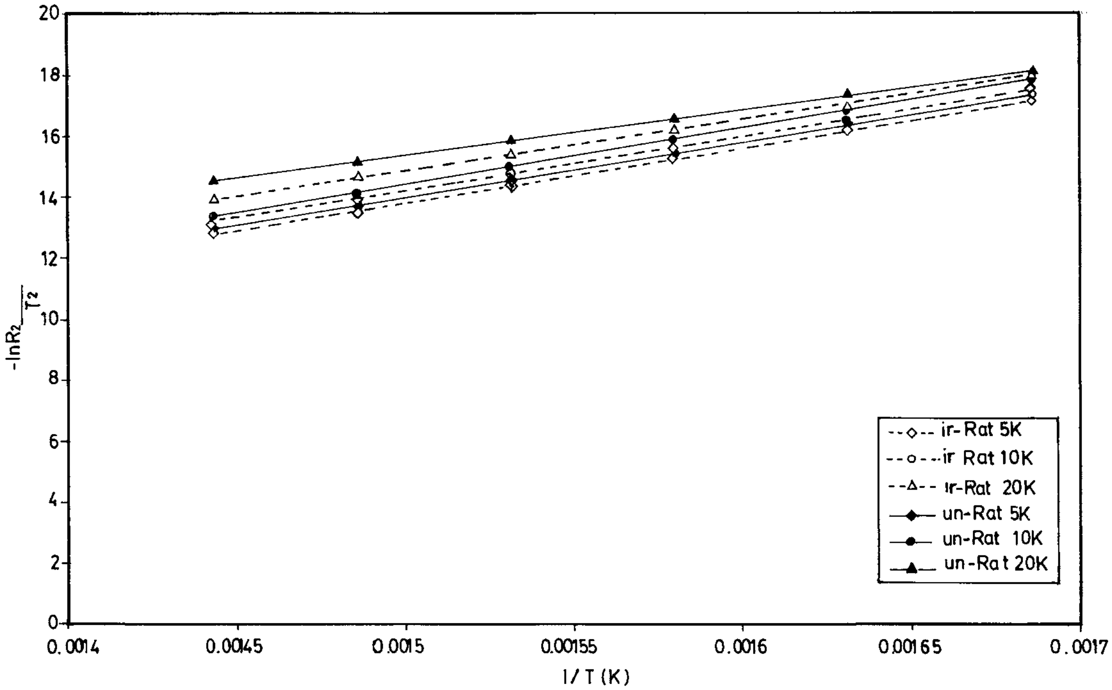


Fig. 5. Isothermal decomposition of gadolinium acetate according to the two-dimensional phase–boundary reaction.

be crystal defects or reactive radicals that are not necessarily identical with intrinsic nucleation sites but are of comparable reactivity and or more probably evolve by a similar sequence of steps into growth nuclei. More extensive irradiation advances, the onset of decomposition; this is envisaged as being due to the involvement of a small amount of decomposition products, which advances the transformation of all precursor-specialized sites into active growth nuclei. The kinetics of growth of all nuclei are identical. The observed increase in reaction rate for γ-irradiated samples is ascribed to a direct relationship between the extent of salt γ-irradiation and number of nuclei developed on subsequent decomposition [16].

Table 3
$\Delta H^{\#0}$ and $\Delta S^{\#0}$ values for isothermal decomposition of gadolinium acetate

Gadolinium acetate	$\Delta S^{\#0}$ (kJ mol^{-1} K^{-1})	$\Delta H^{\#0}$ (kJ mol^{-1})
Un-irradiated	−0.197	145.21
γ-Irradiated (6.07 × 10^6 Gy)	−0.1971	170.90

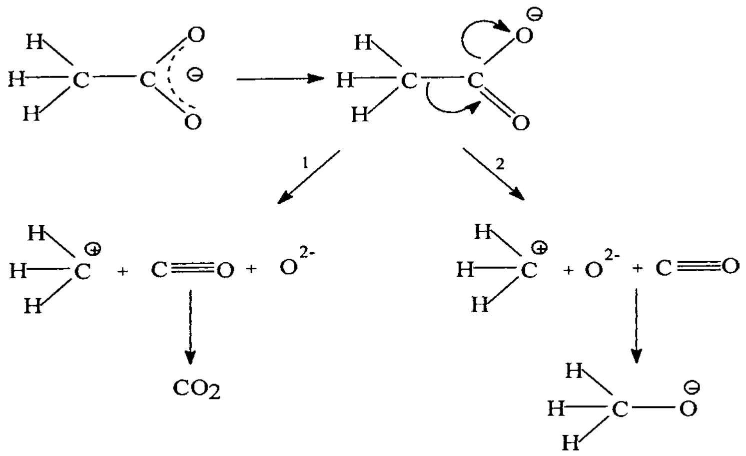
5. Conclusion

In the present investigation, γ-irradiation effects on the thermal decomposition of hydrated gadolinium acetate was studied in air using both isothermal and dynamic techniques. Different theories of solid-state reactions and models were applied to choose the best model or solid-state reaction, which control the decomposition of gadolinium acetate. The effects of γ-irradiation on the decomposition process were studied by irradiating the investigated gadolinium acetate sample to γ-ray doses 10^6 Gy. The kinetic parameters of the decomposition before and after γ-irradiation using isothermal and non-isothermal techniques were calculated and evaluated. The general conclusion of the present study could be summarized in the following:

1. Under isothermal and non-isothermal (dynamic) condition the decomposition of both pristine and pre-irradiated hydrated gadolinium acetate was controlled by phase–boundary model.
2. The kinetic and thermodynamics values of the decomposition process of γ-irradiated gadolinium

acetate were lower than the corresponding values calculated for un-irradiated salt with no change in the applied kinetic function $g(\alpha)$. The radiation retards the thermal process and inhibits the rate of decomposition due to the formation of long lived trapped radicals and holes in the host lattice. The kinetic function used $g(\alpha)$ for isothermal decomposition of un-irradiated and γ-irradiated gadolinium acetate was, however, different from the function used for dynamic decomposition. The general disadvantage of dynamic thermal analysis is the fact that in many cases more, than one function from $g(\alpha)$ fits the experimental results. The selection of a proper model is then practically impossible leading to inability to estimate the real kinetic parameters (E, A). Recently, the view that the combined used of isothermal and non-isothermal methods for kinetic determination is the proper solution has been more and more frequently expressed.

3. The following mechanism could be suggested to explain the decomposition process and the formation of gaseous products. The main step in the suggested mechanism is the rupture of C–O and C–C bonds followed by electronic rearrangement.



Acknowledgements

Financial support by Saudi Basic Industries Corporation (SABC) is greatly acknowledged.

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