

## Kinetic analysis of The Thermal Decomposition of Pristine and $\gamma$ -Irradiated Cadmium Acetate

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**Abstract.** The kinetics of the thermal decomposition of un-irradiated (pristine) and pre- $\gamma$ -irradiated anhydrous cadmium acetate was studied in the temperature range (298-773 K) and in air using isothermal and dynamic 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 decomposition for acceleratory stage was governed by two dimensional phase boundary movement ( $R_2$ ) while in non-isothermal (dynamic) decomposition the kinetic was controlled by nucleation and growth model with two dimensional growth ( $A_2$ ) for un-irradiated and three dimensional growth ( $A_3$ ) for  $\gamma$ -irradiated cadmium acetate. The activation energies of the main decomposition process for un-irradiated and pre- $\gamma$ -irradiated samples were calculated and the results of the isothermal and dynamic integral methods were compared and discussed. The change in texture and crystal structure of the investigated cadmium acetate by  $\gamma$ -irradiation was studied using electron microscopy and X-ray diffraction technique

### Experimental

Cadmium acetate (BDH, England) was used without further purification. The sample used for investigation was dried at 200°C in a muffle furnace to ensure complete dehydration.

The investigated sample weights were in the range of 100 mg. The decomposition was followed in air using isothermal and dynamic thermogravimetric techniques in the temperature range (298-773 K) using Netzsch STA 429, thermal analyzer, (Germany). For isothermal measurement the heating rate was (5° C/min), while under non-isothermal conditions three different heating rates 5° C/min, 10° C/min and 20° C/min were applied (Spinks J.W.T. and Woods R.J. 1990).

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  $\gamma$ -ray cell 220 (Nordion INT-INC, Intario, Canada) at a dose rate of 10<sup>4</sup> 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 (Spinks J.W.T. and Woods R.J. 1990).

### Results and Discussion

Figure 1 shows thermogravimetry (TG) and differential thermal analysis (DTA) curves of the thermal decomposition of cadmium acetate in air. The TG curve shows that the decomposition of Cd(CH<sub>3</sub>COO)<sub>2</sub> takes place in one major step accompanied by an endothermic peak at 573 K corresponding to formation of CdO and volatile products. The weight loss was estimated to be about (47%) of the total weight in good agreement with the theoretical calculated value (48%).

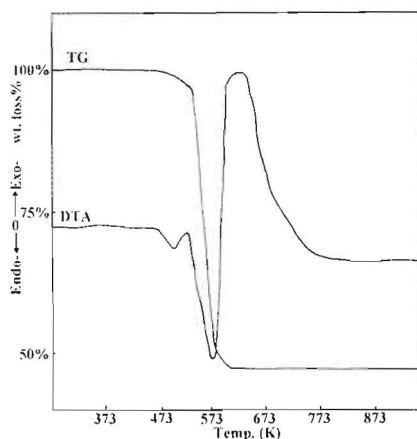


Fig. 1. TG and DTA of cadmium acetate.

### Isothermal Decomposition -

Isothermal decomposition of cadmium acetate was studied in the temperature range (533-543 K). The isothermal  $\alpha/t$  data for the main process i.e. the acceleratory region of dehydrated cadmium acetate decomposition ( $0.05 < \alpha < 0.99$ ) were analyzed according to the various kinetic mechanisms cited in Table 1 (Monshi, M.A.S., et al, 1999). Fig. 2 shows  $\alpha/t$  curves of the isothermal decomposition of un-irradiated and pre- $\gamma$ -irradiated dehydrated cadmium acetate with  $2.5 \times 10^7$  Gy total dose at three different decomposition temperatures (533, 538 and 543 K), where  $\alpha$  is the fraction decomposed at the decomposition time  $t$ . The curves show an increase in the fraction decomposed ( $\alpha$ ) with an increase in the decomposition time up to a maximum value ( $\alpha_{max}$ ) depending on the investigated temperature. In general the isothermal decomposition of both un-irradiated and pre- $\gamma$ -irradiated material produces sigmoid  $\alpha$  vs.  $t$  curves in the range (533-543 K).

Table 1. Mechanistic equation examined in this work.

Equation	Function	Function
One-dimensional diffusion	$\alpha^2$	D <sub>1</sub>
Two-dimensional diffusion	$(1-\alpha)\ln(1-\alpha)+\alpha$	D <sub>2</sub>
Jander equation, three-dimensional diffusion	$[1-(1-\alpha)^{1/3}]^2$	D <sub>3</sub>
Ginstling-Brounshtein equation three-dimensional diffusion	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	D <sub>4</sub>
Two-dimensional phase-boundary reaction	$1-(1-\alpha)^{1/2}$	R <sub>2</sub>
Three-dimensional phase-boundary reaction	$1-\ln(1-\alpha)^{1/3}$	R <sub>3</sub>
First-order kinetic	$\ln(1-\alpha)$	F <sub>1</sub>
Prout-Thompkins branching nuclei	$\ln[\alpha/(1-\alpha)]$	A <sub>1</sub>
Random nucleation: Avrami equation	$-\ln(1-\alpha)^{1/2}$	A <sub>2</sub>
Random nucleation: Erofe'ev equation	$-\ln(1-\alpha)^{1/3}$	A <sub>3</sub>

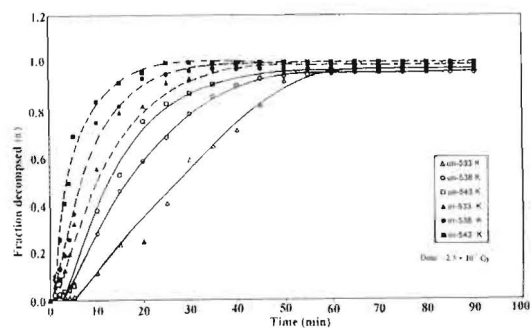
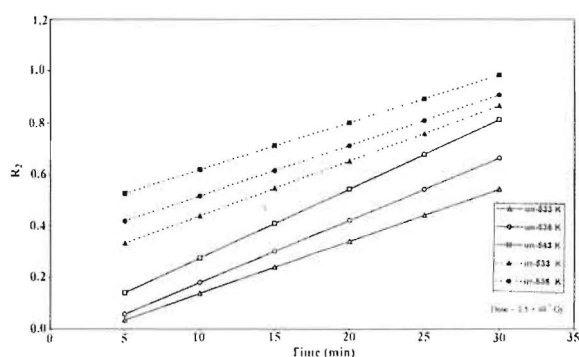


Fig.2. Fractional decomposition  $\alpha$  vs time curves for the isothermal decomposition of cadmium acetate

Under isothermal conditions, the rate constant  $k$ , is independent of the reaction time and so  $kt = g(\alpha)$ . A plot of  $g(\alpha)$  vs  $t$  should give a straight line if the correct form of  $g(\alpha)$  vs  $t$  is reached. The function  $g(\alpha)$  depends on the mechanism controlling the reaction, the size and shape of the reacting particles (Sharp, J.H., et al, 1966). In a diffusion-controlled reaction: D<sub>1</sub> is the function for a one-dimensional diffusion process governed by a parabolic law, with constant diffusion coefficient; D<sub>2</sub> is for a two-dimensional diffusion-controlled process into a cylinder; D<sub>3</sub> is Jander's equation for diffusion-controlled reaction in a sphere and D<sub>4</sub> is a function for a diffusion-controlled reaction starting on the exterior 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  $\alpha$  and  $t$  is the R<sub>2</sub> function for a circular disc reacting from the edge inward and the function R<sub>3</sub> for a sphere reacting from the surface inward. If the solid-state reaction follows first order kinetic (F<sub>1</sub> 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 function A<sub>2</sub> and A<sub>3</sub>, respectively (Gadalla, A. M. 1984). Our results show that isothermal data of cadmium acetate samples obey two-dimensional phase-boundary (R<sub>2</sub>) reaction models (Fig. 3).



**Fig.3. Isothermal decomposition curves for cadmium acetate**

Kinetic energy of the main decomposition processes i.e. the acceleratory region for un-irradiated and pre- $\gamma$ -irradiated material was calculated by applying the least square method using Arrhenius equation and the results are tabulated in Table (2).

**Table 2. Kinetic parameters of the isothermal and non-isothermal decomposition of un-irradiated and ( $\gamma$ -irradiated) cadmium acetate ( $2.5 \times 10^7$  Gy total  $\gamma$ -ray dose)**

Kinetic parameters	Isothermal technique	(Non- Isothermal technique) Heating rate		
		5°C/min	10°C/min	20°C/min
Ea (kJ mol <sup>-1</sup> )	101.8 (1.31)	101.0 (15.1)	96.8 (8.73)	45.0 (6.45)
ln A (min <sup>-1</sup> )	18.9 (4.3)	4.88 (10.19)	7.66 (11.26)	8.79 (11.73)

**Non isothermal Decomposition-**

In the analysis of dynamic TG curves, the temperature rate is set to a constant value  $\beta$  and the function  $g(\alpha)$  is given by Doyle's equation (Doyle, C.D. 1961)

$$g(\alpha) = (A/B) \int_0^t \exp(-E/RT) dT = \frac{AE}{R\beta} P(x)$$

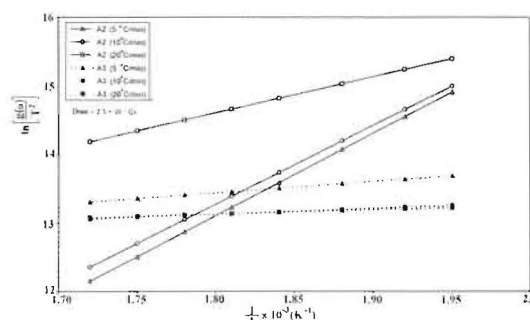
The function P(x) is defined as

$$P(x) = \frac{e^{-x}}{x} - \int_x^\infty \frac{e^{-u}}{u} du$$

where  $u = E/RT$  and  $x$  is the corresponding value of  $u$  which is a fraction  $\alpha$  of material that has decomposed. In the modified Coats- Redfern (Coats, A.W. and Redfern, J. P. 1964) method, the function  $g(\alpha)$  is approximated to the form:

$$\log \left( \frac{g(\alpha)}{T^2} \right) = \log \left( \frac{AR}{EB} \right) - \left( \frac{E}{2.3RT} \right)$$

Accordingly,  $\log [g(\alpha)/T^2]$  is to be calculated for all possible mechanisms cited in Table (1) and plotted against  $1/T$ . The best straight line obtained using LR analysis determines the operating mechanism.  $E_a$  and A can be calculated from the slope and intercept. Fig. (4) shows the results of data analysis performed according to Coats and Redfern equation. The results indicated that the best fit of data was achieved using random nucleation (Avrami-Erofe'ev equation) reaction model  $A_2$ ,  $A_3$  for non-irradiated and pre- $\gamma$ -irradiated samples, respectively. In comparison with isothermal data analysis, there is a change in the mechanism of decomposition from phase boundary reaction proposed for isothermal decomposition to nucleation growth mechanism for non-isothermal decomposition. The general disadvantage of dynamic thermal analysis is the fact that in many cases more than one function  $g(\alpha)$  fits the experimental results and accordingly different kinetic data ( $E_a$ , ln A) could be obtained compared with the data derived from isothermal analysis as reported in the present study. The selection of proper model is then practically impossible leading to inability to estimate the real kinetic parameters ( $E_a$ , ln A). Recently, the view that the combined use of isothermal and non-isothermal methods for thermal data kinetic analysis as the proper solution has been more and more frequently expressed.



**Fig. 4. Dynamic decomposition of cadmium acetate according to the  $A_2$  (un-irradiated) and the  $A_3$  ( $\gamma$ -irradiated) samples by Coats and Redfern method.**

The calculated kinetic parameter using dynamic thermogravimetric techniques are tabulated in Table (2). Both isothermal and non-isothermal data of  $\gamma$ -irradiated cadmium acetate show a significant decrease in the kinetic parameters ( $E_a$ , ln A) of the main decomposition process compared with the data obtained for un-irradiated cadmium acetate. Radiation damage in the host lattice of cadmium acetate generates additional decomposition center that accelerates the rate of all decomposition stages (induction period, acceleratory region and decays

stages) and subsequently reduces the activation energy of the decomposition. The radiation damage induced by  $\gamma$ -irradiation results also, in a significant reduction of the induction period prior to decomposition. The changes in the textural and morphological structure of the investigated samples before and after  $\gamma$ -irradiation were investigated by scanning microscopy (SEM) and X-ray diffraction powder pattern (XDR) technique. The results are presented in Figs. (5 & 6). SEM and XRD measurements for un-irradiated and  $\gamma$ -irradiated cadmium acetate indicate that the sample up to irradiated ( $2.5 \times 10^7$  Gy) dose has largely maintained its crystallographic identity without big changes in the crystals structure by exposure to  $\gamma$ -irradiation prior to thermal decomposition studies.

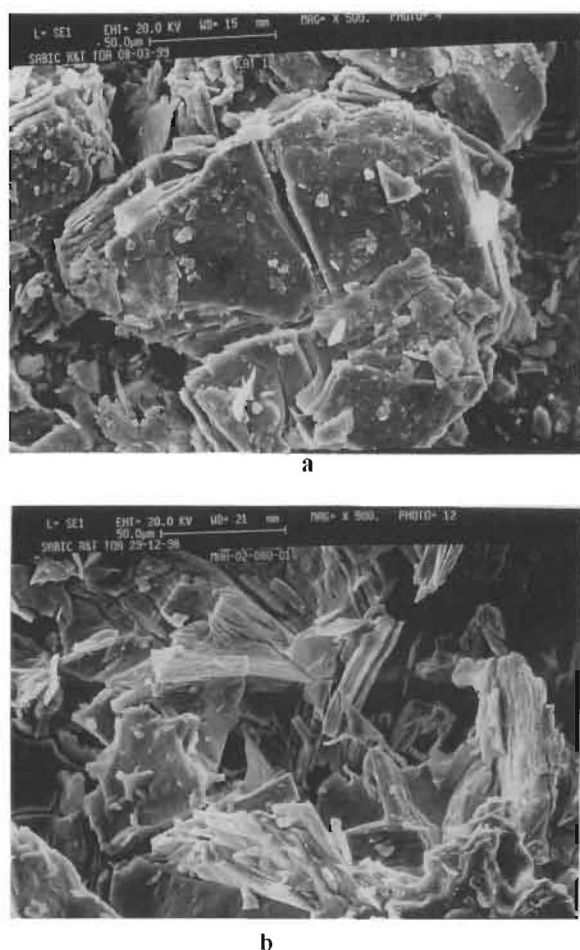


Fig. 5. SEM for cadmium acetate (a) un-irradiated and (b)  $\gamma$ -irradiated ( $2.5 \times 10^7$  Gy).

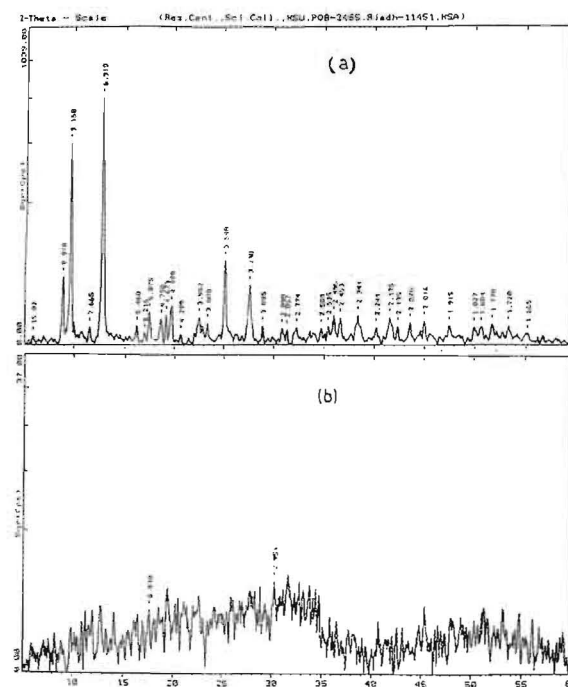


Fig. 6. XRD for cadmium acetate a) un-irradiated and b)  $\gamma$ -irradiated ( $2.5 \times 10^7$  Gy).

### Mechanism of Decomposition

In general, the mechanism of the decomposition of solids could be:- (i) electron transfer (ii) proton transfer (iii) breaks down of the anion or bond scission. Electron transfer operates mainly at low temperatures while at high temperatures proton transfer and bond rupture dominate. Thermal decomposition of cadmium acetate under the present experimental conditions showed that the rate of reaction in the acceleratory region initially increases with time until a maximum is attained. Anion break down is envisaged as proceeding through a catalytic-type process on the surfaces of the oxidic cadmium particles that constitute the active advancing interfaces. The decomposition thereafter proceeds by diffusion-controlled process according to the isothermal investigation for both un-irradiated and pre- $\gamma$  irradiated samples of cadmium acetate.

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 leading to formation of either CO, CO<sub>2</sub>, O<sup>2-</sup> and CH<sub>3</sub>O<sup>-</sup> as depicted below .

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