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Kinetics analysis for non-isothermal decomposition γ -irradiated indium acetate

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Abstract Kinetics analysis for non-isothermal decomposition of un-irradiated and pre- γ -irradiated anhydrous indium acetate was studied in the temperature range (298–1273 K) in static air using dynamics thermogravimetric techniques. The data were analyzed using various solid state reaction models. Integral method using Coats–Redfern equation was applied in dynamic data analysis. The results showed that the kinetic of non-isothermal (dynamic) decomposition was controlled by phase boundary process. The activation energies for un-irradiated and pre- γ -irradiated anhydrous indium acetate were calculated and evaluated.

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1. Introduction

Thermal decomposition of solids is an important field of solid state chemistry with wide technical applications (Brown et al., 1980). However, details of the kinetics were not reported (Levy and Herley, 1971). Previous work on the thermal decomposition of metal acetates indicated that the isothermal decomposition kinetics could be affected markedly by prior exposure to ionizing radiation (Monshi et al., 1998,1999; Alshehri et al., 2000; Mahfouz et al., 2000).

In this investigation, the kinetics of non-isothermal decomposition of anhydrous indium acetate before and after

γ -irradiated was studied by dynamic thermogravimetry. The study also aims to investigate the mechanistic model of decomposition and the kinetic values of the main decomposition process in view of the behaviour of indium acetate as an economic catalyst.

2. Experimental

Indium 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 dynamic thermogravimetric techniques in the temperature range (298–1273 K) using TGA-1, Perkin–Elmer. Three different heating rates 2, 5, and 10 °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 ^{60}Co γ -ray cell 220 (Nordion INT-INC, Intario, Canada) at a dose rate of 10^4 Gy/h. The source was calibrated against Fricke ferrous

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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 and Woods, 1990).

3. Results and discussion

Fig. 1 shows thermogravimetry (TG) and differential thermal analysis (DTA) curves of the thermal decomposition of indium acetate in air. The TG curve shows that the decomposition of $\text{In}(\text{CH}_3\text{COO})_3$ takes place in one major step accompanied by an endothermic peak at 523 K corresponding to the formation of In_2O_3 and some volatile products. The weight loss was estimated to be about (46.66%) of the total weight which is in good agreement with the theoretical calculated value (47.56%).

3.1. Non-isothermal decomposition

Non-isothermal decomposition of un-irradiated and pre- γ -irradiated indium acetate sample is shown in Fig. 2. The rate is set to a constant value β and the function $g(\alpha)$ is given by Doyle's equation (Doyle, 1961)

$$g(\alpha) = \left(\frac{A}{B}\right) \int_0^T \exp \left[\frac{-E}{RT} \right] dT = \frac{AE}{R\beta} p(x)$$

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

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

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

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

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. E_a and A values are calculated from the slop and intercept (Coats and Redfern, 1964). Fig. 3 shows the results of data analysis performed according to Coats–Redfern equation. The results indicate that the best fit of dynamic data of indium acetate was achieved using two-dimensional phase-boundary reaction model (R_2) as listed in Table 1. Trapped electrons and radicals in the host lattice of γ -irradiated indium acetate retard the decomposition process and reduce the number of reactive sites available for the decomposition. The calculated kinetic parameters for the non-isothermal decomposition of indium acetate are listed in Table 2. No significant changes were detected in the calculated kinetic parameters as a result of gamma irradiation.

3.2. Role of irradiation

Upon irradiation with ^{60}Co γ -rays, the Compton effect has the largest cross-section in very light elements and diminishes to zero around atomic number 125 (Eyring, 1935). The possibility of displacement of indium (atomic weight 114.8) by Compton electrons is very low. Generation additional sites of potential nucleation are produced by γ -rays. These may be crystal defect or reactive radicals that are not necessarily identical with intrinsic nucleation sites but are of comparable reactivity and probably evolve (not clear) 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 advance the transformation of all precursor specialized sites into active growth nuclei. The kinetics of growth of all nuclei is identical. The observed increase in reaction rate for γ -irradiated samples is ascribed to direct relationship between the extent of salt γ -irradiation and number of nuclei developed on subsequent decomposition (Galwey et al., 1988; Al Resayes, in press).

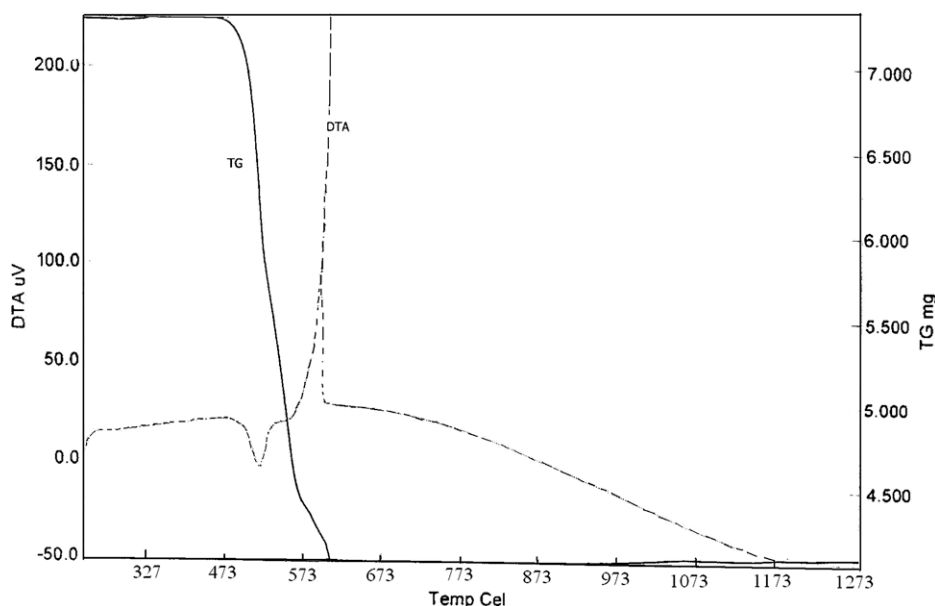


Figure 1 TG and DTA of indium acetate.

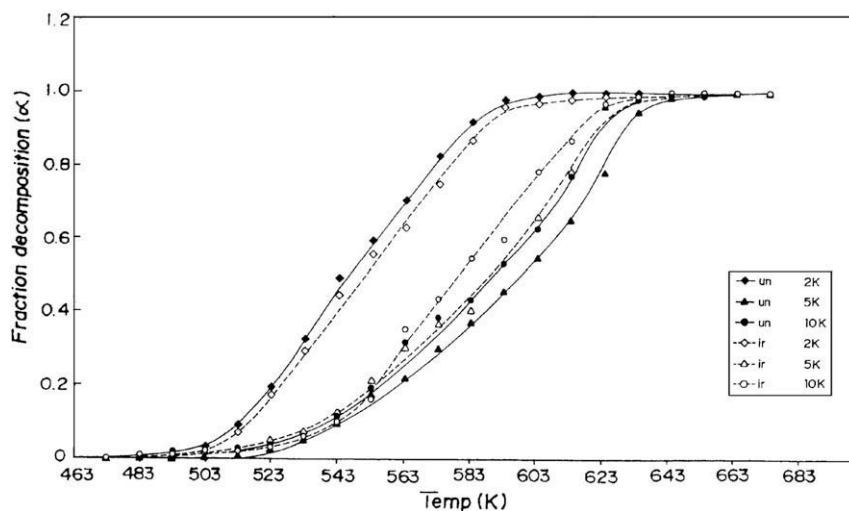


Figure 2 Dynamic measurements for indium acetate thermal decomposition.

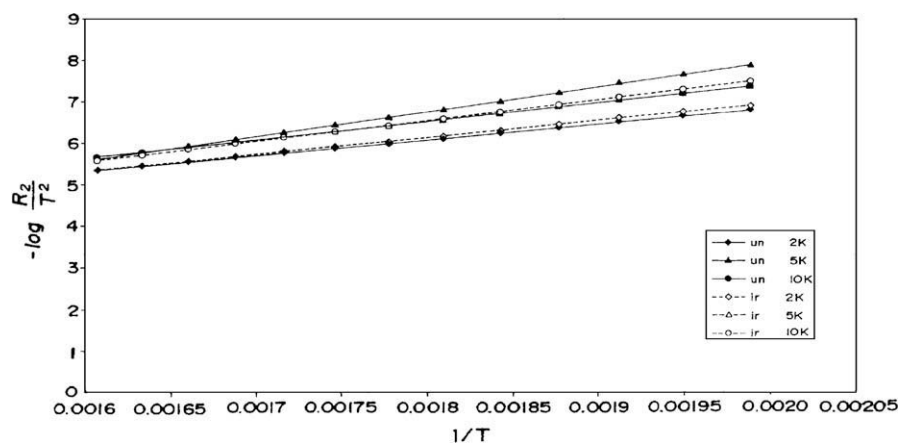


Figure 3 Non-isothermal decomposition of indium acetate according to the two-dimensional phase-boundary reaction.

Table 1 Mechanistic equations 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	$1 - \ln(1 - \alpha)^{1/3}$	R_3
First-order kinetic	$\ln(1 - \alpha)$	F_1
Prout–Thompkins branching nuclei	$\ln[\alpha/(1 - \alpha)]$	A_1
Random nucleation: Avrami equation	$-\ln(1 - \alpha)^{1/2}$	A_2
Random nucleation: Erofe'ev equation	$-\ln(1 - \alpha)^{1/3}$	A_3

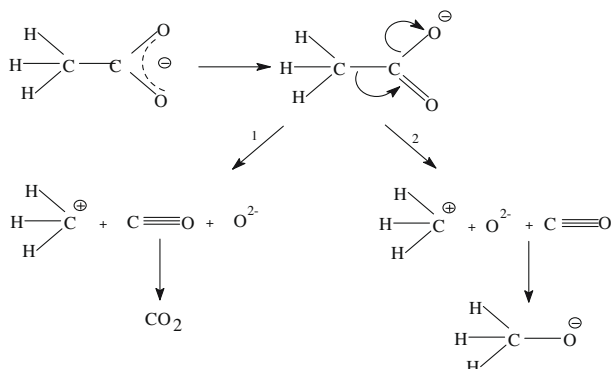
Table 2 Activation energy of non-isothermal decomposition of indium acetate.

Kinetic parameters	Non-isothermal technique		
	Heating rate ($^{\circ}\text{C}/\text{min}$)		
	2	5	10
E_a kJ mol^{-1} (un-irradiated)	82.37	89.13	95.27
E_a kJ mol^{-1} (irradiated)	86.82	94.53	103.74

3.3. 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 indium 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 indium particles that constitute the active advancing interfaces. The decomposition thereafter proceeds by two-dimensional phase-boundary reaction according to the non-isothermal investigation for both un-irradiated and pre- γ -irradiated samples of indium 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.

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