Isothermal decomposition of γ-irradiated thallous acetate

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Abstract

Isothermal decomposition of non-irradiated and post-γ-irradiated thallous acetate has been investigated at different temperatures between 553 and 583 K. Irradiation was observed to enhance the rate of decomposition without modifying the mechanism of thermal decomposition. Thermal decomposition of thallous acetate has been shown to proceed by nucleation and growth mechanism (Avrami and Erofe'ev equation) both for non-irradiated and post-γ-irradiated samples. The enhancement of the decomposition was found to increase with an increase in the γ-ray dose applied to the sample and may be attributed to an increase in point defects and formation of additional nucleation centers generated in the host lattice. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Thermal decomposition of solids is an important field of solid state chemistry with wide technical applications [1]. Many recent studies on the isothermal decomposition of inorganic solids have included measurements on samples that were exposed to radiation prior to heating. These measurements were performed for one or both of the following reasons. Firstly, the material may have been irradiated to investigate one or more features of the decomposition process. Secondly, it may have been included in a 'radiation damage' study to determine if radiation can modify one or more properties of the material in an important way by creating point defects or increasing the number of nucleation forming sites [2].

In this investigation, the kinetics of the thermal decomposition of thallous acetate before and after γ-irradiation have been studied by isothermal thermo-

gravimetry. No previous study of this type have been made on thallous acetate.

2. Experimental

Thallous acetate was obtained commercially (BDH, England) and used without further purification. The decomposition of thallous acetate in air yields Tl_2O_3 and volatile products. Within experimental error, the reaction eventually goes to completion. The decomposition was followed using an isothermal thermogravimetric technique in the temperature range of (553–583 K) using a Netzsch STA 429, thermal analyzer (Germany). The heating rate used was (5°C/min). The sample weights were about 100 mg. Four irradiation samples were encapsulated in glass vials under vacuum and exposed to successively increasing doses of radiation at a constant flux using a Co-60 γ-ray cell 220 (Nordion INT-INC, Ontario, Canada). The dose rate was 10^4 Gy/h. The source was calibrated against a Fricke Ferrous sulphate dosimeter. The dose

rate in the irradiated samples was calculated by applying appropriate corrections for photon mass attenuation and energy absorption in the sample and the dosimeter solution [3].

3. Results and discussion

Fig. 1 show thermogravimetry (TG) and differential thermal analysis (DTA) of the thermal decomposition of thallous acetate in air. The TG curve shows that decomposition of CH_3COO Tl takes place in one step and commences at 260°C. The weight loss observed was ~20%, which is in agreement with the theoretically calculated value assuming the formation of Tl_2O_3 as final products. Thermal decompositions of non-irradiated and post-irradiated samples of thallous acetate with total γ-ray dose of 6.07×10^6 Gy were studied in the temperature range 553–583 K. The general form is sigmoidal for both non-irradiated
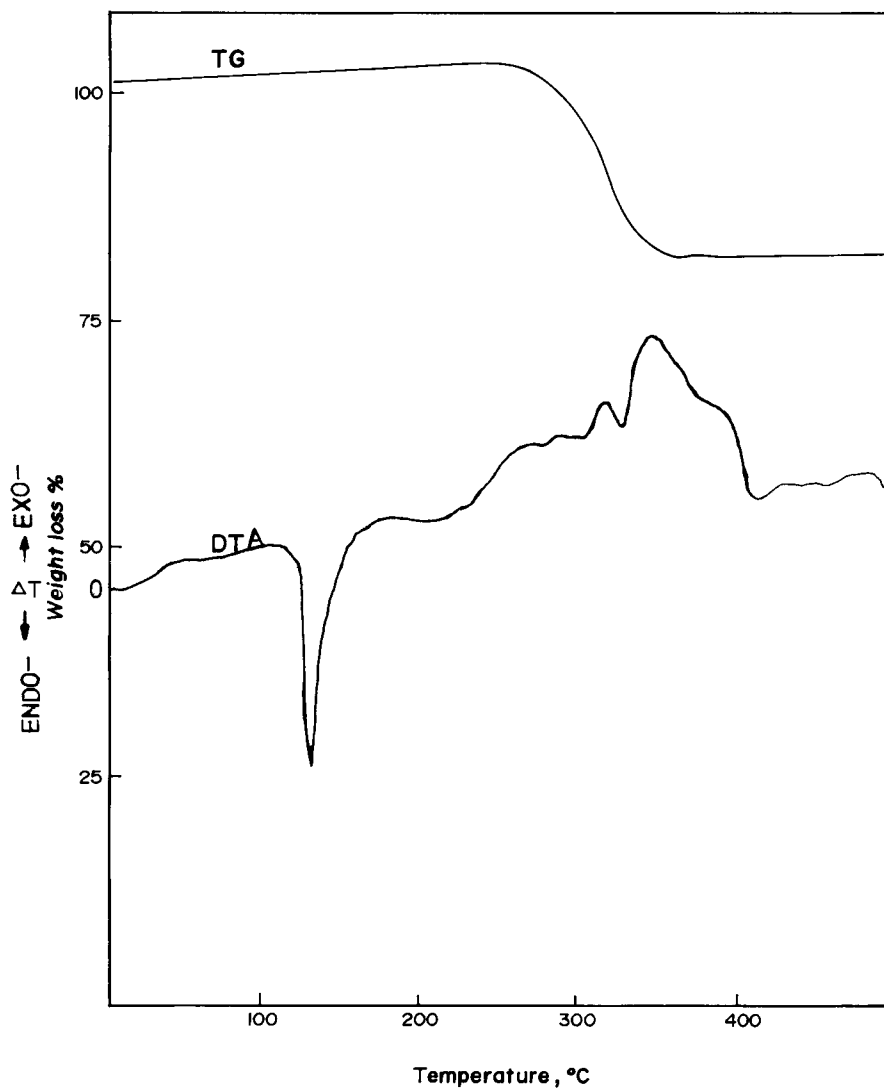

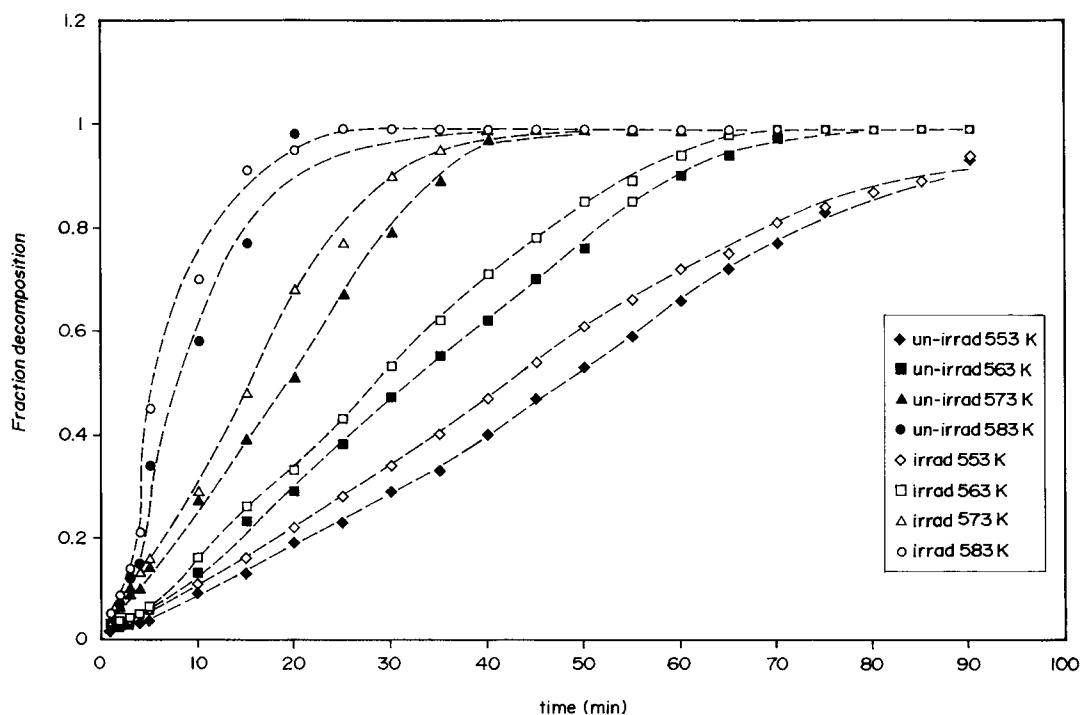Fig. 1. The TG and DTG of thallous acetate.

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

and post-irradiated samples with a gradual approach to the acceleratory region (see Fig. 2). The α-time curves for the-irradiated samples showed that the time required to reach the maximum rate proceeds faster, as the value of α at the point of inflection, i.e. α_{max} is reduced and the induction period was shorten by irradiation[1]. The observed promotion of decomposition by post-irradiation is ascribed to the generation of additional sites of potential nucleation as crystal defects or long-lived reactive radicals may be of different kind compared to intrinsic nucleation sites but are of comparable activity. The isothermal α/t data for the main process, i.e. the acceleratory region of thallous acetate decomposition ($0.017 < \alpha < 0.95$) were analyzed according to the various kinetic mechanism cited in Table 1 [4]. Under isothermal conditions, the rate constant k is independent of reaction time and so $kt \propto g(\alpha)$. A plot of $g(\alpha)$ versus t should give a straight line if the correct form of $g(\alpha)$ versus t is selected. The

function $g(\alpha)$ depend on the mechanism controlling the reaction and on the size and shape of the reacting particles [5]. In a diffusion-controlled reaction: D is the function for a one-dimensional diffusion process governed by a parabolic law, with constant diffusion coefficient. The function D_2 is for a two-dimensional diffusion-controlled process into a cylinder. The function 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 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 kinetics, (F_1 function) then the rate determining step is the nucleation process and there is equal probability of nucleation at each active site. In a phase-boundary reaction, it is assumed that the nucleation step occurs instantaneously, so that the

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[1] α is the measure of the conversion [$\alpha = (M_o - M)/(M_o - M_f)$, M_o, M, M_f are initial, actual and final sample masses, respectively].

Table 1
Mechanistic equation examined in this work

Equation	Function, $g(\alpha)$	Function
One-dimensional diffusion	α^2	D_1
Two-dimensional diffusion	$\alpha + (1-\alpha)\ln(1-\alpha)$	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
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

surface of each particle is covered with a layer of 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_2 and A_3, respectively. Our results show that both sets of data for the non-irradiated and γ-irradiated samples obey the Avrami and Erofe'ev equations, i.e. random nucleation followed by growth of three-dimensional nuclei, (Fig. 3). For the γ-irradiated material, some radiolysis of thallous acetate occurs. The gas produced is evolved in part into the capsule during irradiation
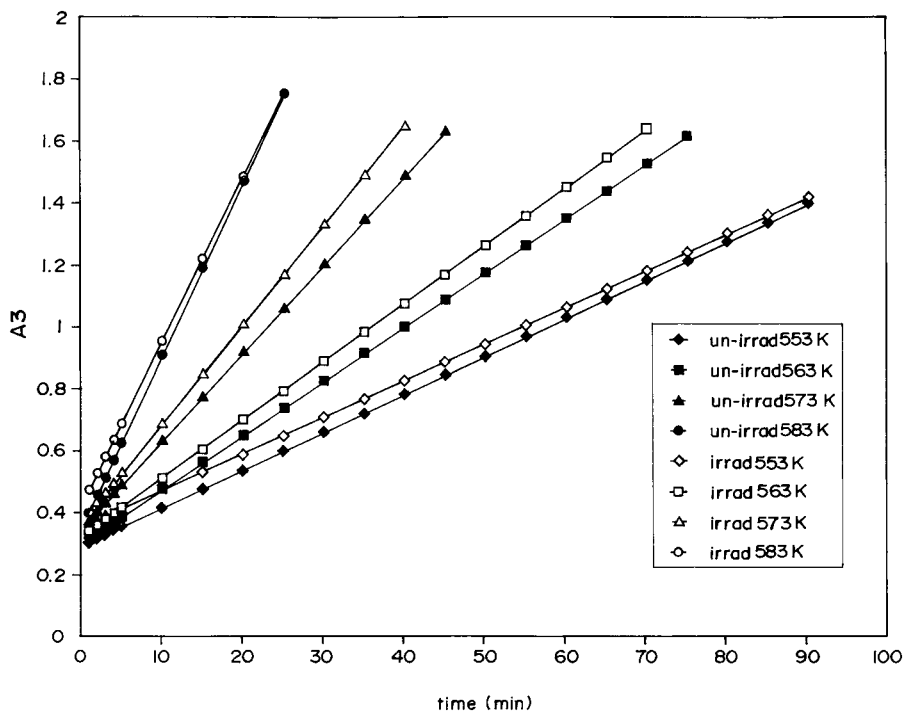

Fig. 3. Isothermal decomposition curves for thallous acetate.

and in part on first heating to the decomposition temperature. This may create additional numbers of potential nucleation forming sites, help to shorten the induction periods and accelerate the decomposition process. The reaction begins at the surface from a number of potential nuclei, which become active by thermal fluctuation. Growth then proceeds three-dimensionally into the crystalline probably along preferred planes. Irradiation appears to increase the number of potential nuclei, but does not enhance the growth rate. The activation energy of the main decomposition process, i.e. the acceleratory region was calculated from least square method using Arrhenius equation as shown in (Fig. 3) and the values were found to be $E=140.65$ kJ mol^{-1} and $E=125.97$ kJ mol^{-1} for the non-irradiated and post-irradiated samples, respectively. It could be seen that γ-irradiation brings about no significant change in the activation energy values of the decomposition reaction. The radiolytic products formed in case of post-irradiated sample allow the decomposition to proceed easier, thereby, lowering the activation energy. The changes in textural and morphological structure of the investigated samples before and after γ-irradiation was investigated by scanning electron microscopy and the results are presented in Fig. 4a and b. The results indicated that the irradiated sample up 6.07×10^6 Gy γ-ray dose has largely maintained its crystallographic identity without significant charges in the crystal structure by exposure to γ-irradiation.

4. Mechanism of decomposition

In general, mechanism of the decomposition of solids could be (i) electron transfer, (ii) proton transfer, (iii) break down of the anion or bond scission [6]. Electron transfer operates mainly at low temperatures while at high temperatures proton transfer and bond rupture predominates. Thermal decomposition of thallous acetate under the present experimental condition 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 metallic thallium particles that constitute the active advancing interfaces. The decomposition thereafter proceeds by a nucleation and growth process for both non-irradiated and post-γ irradiated samples of thallous acetate.

5. Role of irradiation

Upon irradiation with ^{60}Co γ-ray, the Compton effect has the largest cross-section, except for materials of very high atomic number and, moreover, the number of atoms displaced has its maximum in case of light elements and diminishes to zero around atomic number 125 [7]. Irradiation with these rays, therefore, excludes the possibility of displacement of thallium (at. wt. 204.37) by Compton electrons but generates
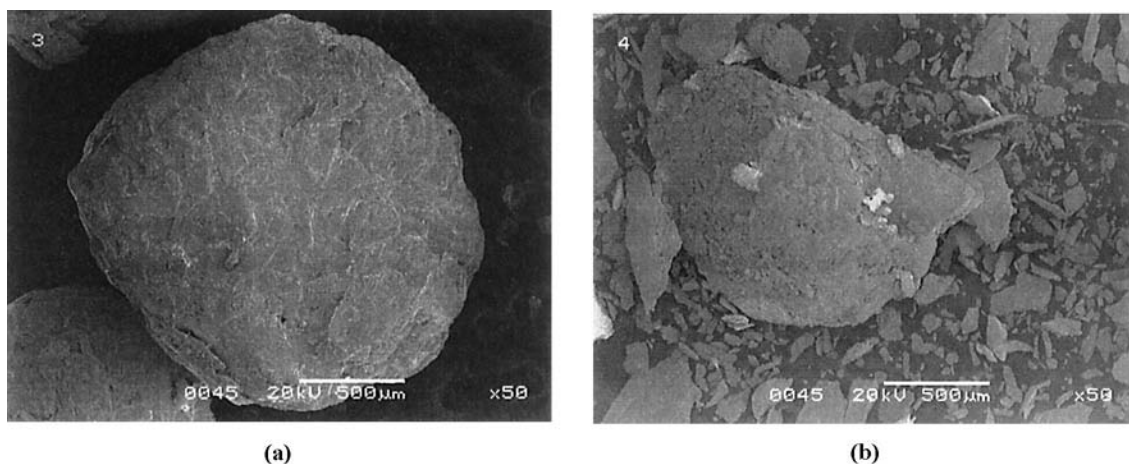

Fig. 4. The SEM and EDX for thallous acetate, (a) non-irradiated, and (b) γ-irradiated (6.07×10^6 Gy).

additional sites of potential nucleation. These may 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 reaction; 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 kinetic 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 [8].

References

[1] W.E. Brown, D. Dollimore, A.K. Galwey, Comprehensive Chemical Kinetic, Vol. 22, Elsevier, Amsterdam, 1980.

[2] P.W. Levy, P.J. Herley, J. Phys. Chem. 75 (1971) 191.

[3] J.W.T. Spinks, R.J. Woods, An Introduction to Radiation Chemistry, Wiley, New York, 1964.

[4] J.H. Sharp, W.G. Bindley, B.N.N. Achar, J. Am. Ceram. Soc. 49 (1966) 379.

[5] A.M. Gadalla, Thermochim. Acta 74 (1984) 255.

[6] L.L. Bircumshow, B.H. Newmann, Proc. R. Soc. London, Ser. A 227 (1954) 115.

[7] R.D. Evans, The Atomic Nucleus, McGraw Hill, New York, 1967.

[8] A.K. Galwey, M.A. Herley Mohamed, J. Chem. Soc., Faraday Trans. 84 (3) (1988) 729.