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THE EFFECT OF γ-IRRADIATION ON THE THERMAL DECOMPOSITION OF LEAD NITRATE

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ABSTRACT

The effect of γ-irradiation on the thermal decomposition of $Pb(NO_3)_2$ has been studied by the gas evolution method. Irradiation enhances the decomposition rate, the effect increasing with dose. Post-irradiation annealing tends to restore the decomposition characteristics of the original unirradiated substance. The data have been analysed using the Prout-Tompkins relationship, the first order rate law and the contracting volume formula.

INTRODUCTION

A considerable amount of work has been done on the thermal decomposition of lead nitrate, using thermogravimetric and gas evolution methods [1–6]. A recent study of the thermal decomposition of γ-irradiated lead nitrate by dynamic thermogravimetry by the present authors [7] has revealed that the decomposition proceeds through three stages. The decomposition of both unirradiated and irradiated $Pb(NO_3)_2$ in each stage follows the Mampel model equation [8], $-\ln(1-\alpha)$ for $g(\alpha)$, and the rate-controlling process is random nucleation with the formation of a nucleus on every particle. The values of activation energy in each stage decrease with increase in irradiation dose. A study of the thermal decomposition of γ-irradiated $Pb(NO_3)_2$ by the gas evolution method has been made by Mohanty and Ray [9] and the data were analysed on the basis of the Prout-Tompkins law. The present paper reports studies on thermal decomposition of γ-irradiated $Pb(NO_3)_2$ by the gas evolution method carried out to investigate the range of applicability of the equations that govern thermal decomposition, and to compare the values of activation energy obtained by these equations with those obtained by thermogravimetric studies.

EXPERIMENTAL

Material

GR grade lead nitrate (E. Merck) was used in the form of fine powder (200–240 Mesh). It was dried in vacuo over P_2O_5.

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Irradiation

Samples of the dried salt, sealed in glass ampoules were irradiated with ^{60}Co γ-rays to different doses between 100 and 400 Mrad at a dose rate of 0.5 Mrad h^{-1}. The irradiated samples were also preserved over P_2O_5 prior to thermal decomposition studies.

Decomposition studies

The decomposition apparatus and the experimental procedure employed were the same as those described earlier [10]. Flurolube HO oil was used as manometric liquid and Kel-F grease as lubricant for stopcocks.

Samples of $Pb(NO_3)_2$ (50 mg) were decomposed in an evacuated (10^{-6} mm Hg) vessel kept in a thermostatically controlled electric furnace at temperature in the range 380–425 °C (±0.5 °C) and the course of the reaction was followed by measuring the total pressure p of the evolved gases at different time intervals t. The final pressure, p_f was obtained by heating at 500 °C till there was no further pressure rise and then cooling to the respective temperature of each run. Decomposition was found to be complete under these conditions. The fractional decomposition $\alpha = p/p_f$ was calculated from these pressure values.

Estimation of damage

The damage NO_2^- produced in each sample was estimated spectrophotometrically [11] with a Beckman model DU_2 instrument.

Isothermal annealing

Irradiated crystals were annealed in air isothermally at 160 ± 0.5 °C in a thermostatic electric hot air oven for different time intervals upto 100 h. The subsequent thermal decomposition behaviour of the partially pre-annealed samples was studied at 400 °C.

RESULTS AND DISCUSSION

The chemical damage

The concentration of damage NO_2^- in the irradiated samples is

Dose (Mrad)	100	200	300	400
NO_2^- (p.p.m.)	2000	2336	2822	3167

The concentration of NO_2^- increases with irradiation dose.

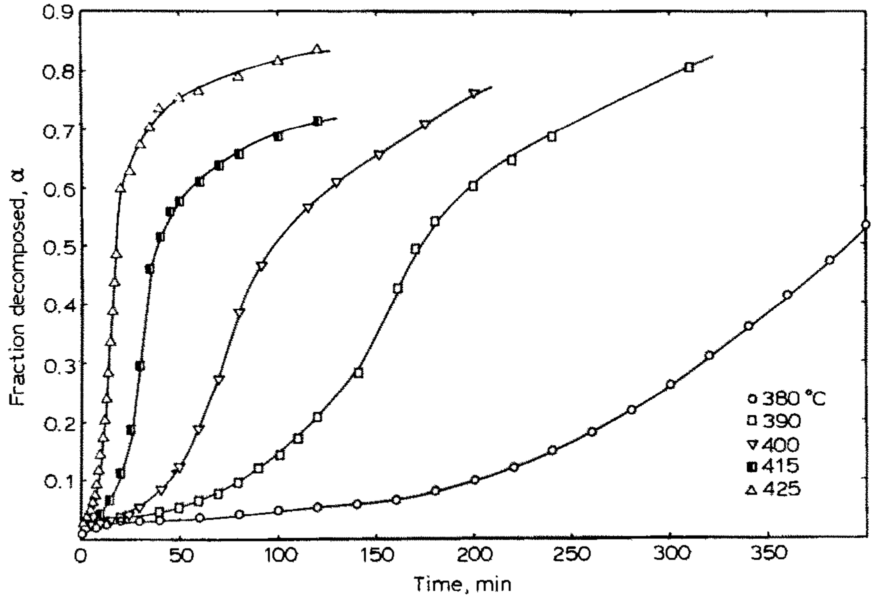

Fig. 1. Thermal decomposition of unirradiated lead nitrate at different temperatures.

The general characteristic of decomposition

The results of isothermal decomposition of unirradiated $Pb(NO_3)_2$ at different temperatures between 380 and 425 °C and those of the samples irradiated to 100 and 400 Mrad γ-rays are presented in Figs. 1, 2 and 3, respectively. The $(\alpha-t)$ curves are sigmoid in nature, and are characteristic of autocatalytic type reactions; the decomposition proceeding through three stages: (i) initial gas evolution, (ii) acceleratory, and (iii) decay stages. Irradiation does not change the shape of the $(\alpha-t)$ plots.

The initial gas evolution was so rapid that it was not possible to determine the kinetics and energetics of the process. In the case of the unirradiated samples, the initial gas evolution is due to physical desorption of gases from the surface, or to escape of occluded gases from the interior of the crystals. The initial gas evolution increases with increase in irradiation dose. This is evident from the fact that the gas evolution occurs only to the extent of $\alpha \simeq 0.02$ at 425 °C for the unirradiated salt, whereas for $Pb(NO_3)_2$ irradiated to 400 Mrad the gas evolution occurs to the extent of $\alpha \simeq 0.141$ at the same temperature. The increase of gas evolution upon irradiation arises from the release of the damage oxygen trapped in the crystals.

The kinetics and energetics of decomposition

The $\alpha-t$ curves have been analysed according to the Prout-Tompkins relationship [12]

$$\log \alpha/(1-\alpha) = k_{1,2}t + C_1 \quad (1)$$

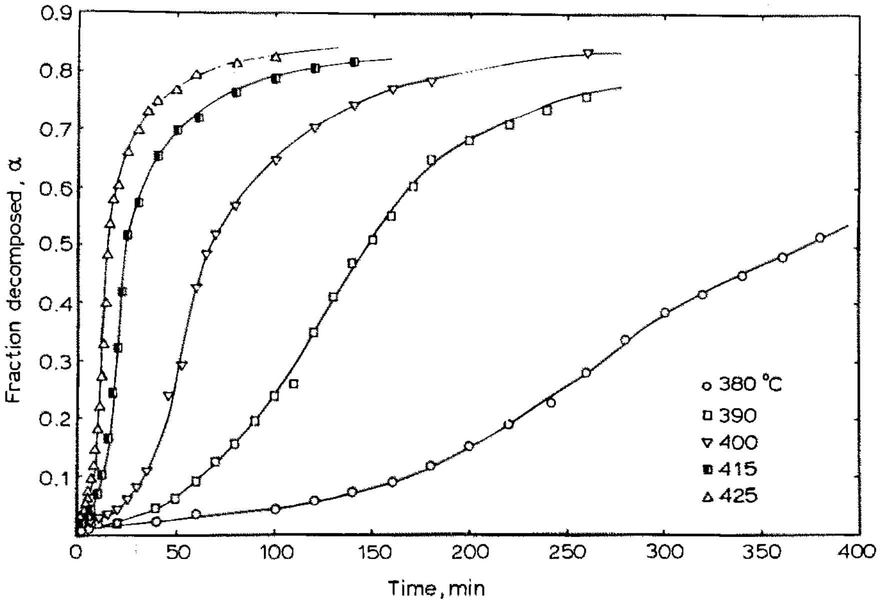

Fig. 2. Thermal decomposition of 100 Mrad γ-irradiated lead nitrate at different temperatures.

the first-order rate law

$$\log 1/(1-\alpha) = k_{3,4}t + C_2 \tag{2}$$

and the contracting volume formula [13]

$$1-(1-\alpha)^{1/3} = k_{5,6}t + C_3 \tag{3}$$

with three different rate constants in each case for the acceleratory (k_1, k_3 and k_5) and the decay (k_2, k_4 and k_6) stages (Table 1). It is found that even with two constants none of the rate laws holds good for the experimen-

TABLE 1

Rate constants at different temperatures

Temperature (°C)	Prout-Tompkins relation						First-order law		
	k_1 (min$^{-1}\times10^2$)			k_2 (min$^{-1}\times10^3$)			k_3 (min$^{-1}\times10^3$)		
	Un-irrad.	100 Mrad	400 Mrad	Un-irrad.	100 Mrad	400 Mrad	Un-irrad.	100 Mrad	400 Mrad
380	0.43	0.58	0.72	–	3.29	2.46	1.36	1.52	1.94
390	1.03	1.06	1.26	4.01	3.66	2.99	3.11	3.84	5.54
400	2.02	2.88	2.28	4.61	4.42	3.25	5.43	4.31	7.97
415	4.91	7.16	3.50	5.50	5.20	4.20	11.96	15.73	14.21
425	9.55	10.37	8.65	6.63	10.43	8.90	32.74	29.90	25.00

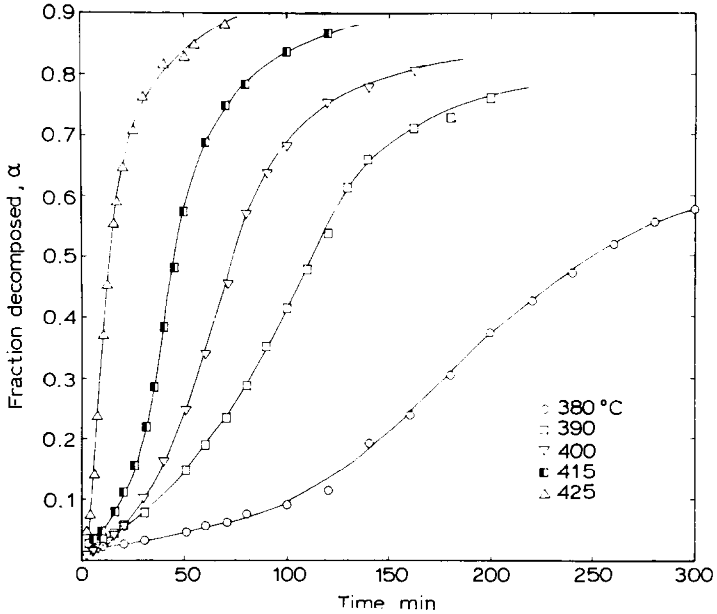

Fig. 3. Thermal decomposition of 400 Mrad γ-irradiated lead nitrate at different temperatures.

tal data over the entire course of the reaction. The range of applicability is $0.010 < \alpha < 0.884$ for the Prout-Tompkins relationship, $0.066 < \alpha < 0.884$ for the first order rate law, and $0.102 < \alpha < 0.884$ for the contracting volume formula.

The Arrhenius plots for the Prout-Tompkins constants k_1 and k_2 are linear and yield activation energies E_1 and E_2 of 254.9 and 53.7 kJ for the acceleratory and decay stages respectively (Table 2). Activation energies calculated from the temperature dependence of the first order k_3 and k_4 are 252.7 and 50.8 kJ and those from k_5 and k_6 of the contracting volume formula are 282.7 and 48.4 kJ respectively.

			Contracting volume formula					
k_4(min^{-1} × 10^3)			k_5(min^{-1} × 10^3)			k_6(min^{-1} × 10^3)		
Un-irrad.	100 Mrad	400 Mrad	Un-irrad.	100 Mrad	400 Mrad	Un-irrad.	100 Mrad	400 Mrad
–	1.46	1.34	0.56	0.74	1.27	–	0.85	0.92
2.95	2.05	2.20	2.42	2.38	3.23	1.44	1.04	1.09
3.29	2.40	2.55	4.16	2.60	4.63	1.70	1.17	1.17
3.83	3.07	5.48	8.64	11.11	8.67	1.95	1.34	1.46
4.78	3.38	8.62	22.63	22.31	14.83	2.39	1.55	3.12

TABLE 2

Activation energies

$Pb(NO_3)_2$	E (kJ mol^{-1}) (gas evolution method)						E (kJ mol^{-1}) (dynamic thermogravimetry: Coats-Redfern equation)		
	Pront-Tompkins		First-order		Contracting volume		Stage I	Stage II	Stage III
	E_1	E_2	E_1	E_2	E_1	E_2			
Unirradiated	254.9	53.7	252.7	50.8	282.7	48.4	296.8	93.9	133.1
	(0.9983)	(0.9946)	(0.9929)	(0.9806)	(0.9802)	(0.9891)			
Irrad. 100 Mrad	253.3	52.3	244.0	56.3	276.7	47.9	279.3	91.6	130.8
	(0.9926)	(0.9963)	(0.9861)	(0.9963)	(0.9842)	(0.9910)			
Irrad. 400 Mrad	196.1	54.8	197.8	49.9	193.6	47.3	211.4	86.7	114.7
	(0.9865)	(0.9912)	(0.9805)	(0.9997)	(0.9872)	(0.9927)			

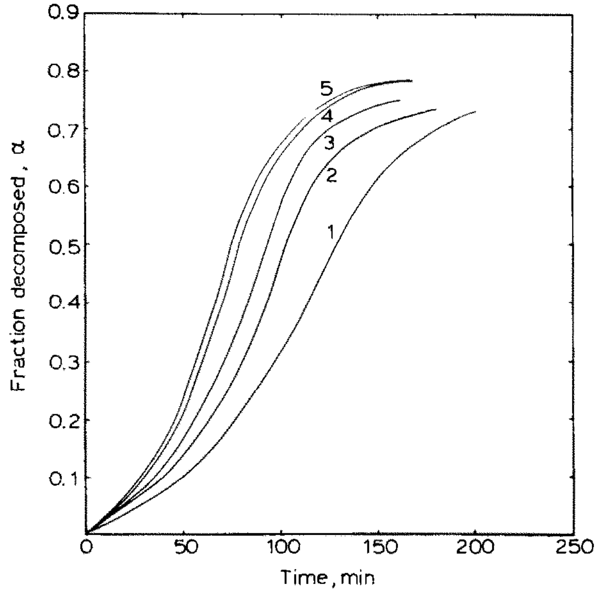

Fig. 4. Effect of γ-irradiation dose on the thermal decomposition of lead nitrate at 400 °C.

Values of E have been obtained by linear regression analysis and the respective correlation coefficients are given in parentheses in Table 2. It is evident from Table 2 that the value of E of the acceleratory stage decreases with increase in irradiation dose while that for the decay stage remains almost unaffected. It is of interest that the agreement between values of activation energy calculated from the three kinetic equations is good, within 10%. Since the change in activation energy upon irradiation is small, it would appear that the same processes govern the decomposition of the unirradiated and the irradiated salt.

TABLE 3

The effect of irradiation on rate constant

Dose (Mrad)	Prout-Tompkins		First-order		Contracting volume	
	k_1 (min^{-1} ×10^2)	k_2 (min^{-1} ×10^3)	k_3 (min^{-1} ×10^3)	k_4 (min^{-1} ×10^3)	k_5 (min^{-1} ×10^3)	k_6 (min^{-1} ×10^3)
0	1.20	1.90	4.83	1.05	2.99	0.60
100	1.45	2.16	6.41	1.54	4.32	0.83
200	1.56	2.29	6.85	1.69	4.14	0.85
300	2.04	2.89	7.68	2.24	4.87	1.04
400	2.12	3.60	7.94	2.77	4.82	1.27

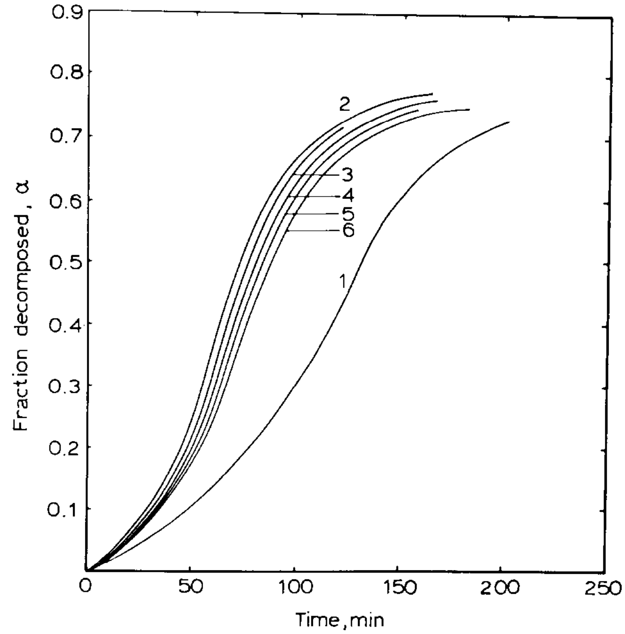

Fig. 5. Effect of pre-annealing on the thermal decomposition of 400 Mrad γ-irradiated lead nitrate at 400 ° C.

The influence of γ-irradiation on the kinetics of thermal decomposition of $Pb(NO_3)_2$ at a given temperature (400 ° C) is illustrated in Fig. 4. The rate constants increase with increase in irradiation dose (Table 3).

Figure 5 shows the effect of partial pre-annealing of the chemical damage on the subsequent thermal decomposition at 400 ° C of the salt irradiated to 400 Mrad. The decomposition characteristics of the irradiated salt tend upon thermal annealing to revert to those of the unirradiated material. The values of k_1, k_3 and k_5 decrease with the time of annealing while those of k_2, k_4 and k_6 remain almost unaffected (Table 4).

TABLE 4

The effect of pre-annealing on the rate constant of the acceleratory and decay stages

Annealing time (h)	Prout-Tompkins		First-order		Contracting volume	
	k_1 (min^{-1} ×10^2)	k_2 (min^{-1} ×10^3)	k_3 (min^{-1} ×10^3)	k_4 (min^{-1} ×10^3)	k_5 (min^{-1} ×10^3)	k_6 (min^{-1} ×10^3)
0	2.21	3.25	7.35	2.55	4.55	1.17
10	2.07	6.38	7.04	4.38	4.87	2.28
25	2.00	7.26	6.76	4.86	4.16	2.58
50	1.99	6.31	6.23	4.33	4.08	2.25
100	1.68	6.59	6.03	4.33	3.83	2.32

A comparison of the values of E obtained by the gas evolution method with those obtained by dynamic thermogravimetric method (Table 2) shows that the E values from the latter method are slightly higher than those from the former method. The E values obtained by the thermogravimetric method for the second and third stages show a decrease with increase in the irradiation dose. However, in the gas evolution method, the E values for the decay stage do not appreciably change with increase of dose.

Chemistry of the decomposition

Baekeland [1] has reported that the decomposition of lead nitrate begins at 205 °C and becomes energetic above 357 °C. According to Thorpe and Whiteley [14] the decomposition begins in vacuo at 283 °C

$$Pb(NO_3)_2 \rightarrow PbO + NO_2 + O_2 \tag{4}$$

Vratny and Gugliotta [4] reported that the decomposition proceeds via a basic nitrate or metallic nitrite structure. A decomposition procedure has also been suggested by Nicol [2]. Thermogravimetric studies by Wendlandt [3] show that the decomposition begins at 370 °C in air with the formation of $Pb_2O(NO_3)_2$ at 435 °C. Mu and Perlmutter [6] observed the decomposition starting at 335 °C at a heating rate of 1 °C min^{-1} in nitrogen atmosphere. Margulis et al. [5] found using DTA and TGA studies that the decomposition begins at 380 °C and occurs in four stages. In the first stage a liquid phase is formed which is due to the formation of a eutectic between $Pb(NO_3)_2$ and $2PbO \cdot Pb(NO_3)_2$ m.p. 407 °C. Thermogravimetric study by the present authors [7] showed that the decomposition begins at 380 °C at a heating rate of 5 °C min^{-1} in air, and that the reaction occurs in three stages.

Mechanism of decomposition

The decomposition of solids is governed by the formation and growth of nuclei which are formed on the external surface of, and to a lesser extent within, the mass of the crystal. In some cases, clustering occurs, and may mean that centres are formed from each other; in others, the appearance of rows of nuclei suggest that there are favoured places, such as along surface cracks or lines of strain, where formation of nuclei is preferred. The reaction is mainly initiated on the external surface, and leads to the formation of an array of product molecules.

The Prout-Tompkins analysis for solid decompositions was derived on the basis of such branching reaction nuclei, i.e. molecules of reactant situated at lattice imperfections mainly on the surface of the solid and possessing a low energy of activation for decomposition.

Acceleration of the decomposition occurs when these branching chain nuclei form reactive planes in the material producing mechanical strain which may result in the actual disruption of the crystals. Eventually these planes interfere with one another, and after the time of maximum velocity the reaction rate is controlled by the number of undecomposed molecules present in the system. Autocatalytic reactions of the Prout-Tompkins type require that all the solid products shall be in a position to catalyse all reactant molecules equally throughout the entire course of the reaction. This is not feasible in a solid because of the low mobility of the reacting constituents. However, in the present case it is valid since a liquid phase is formed [5] in the initial part of the decomposition.

Mechanism of radiation enhancement of thermal decomposition

Several studies on the influence of irradiation on the thermal decomposition of solid substances have been reported [15]. Generally, the effect of irradiation is to increase the velocity constants for both the acceleratory and decay stages. These effects arise from the chemical damage fragments produced by irradiation constituting decomposition nuclei by themselves, or from decomposition nuclei formed as a result of the Wigner energy released on recombination of interstitials and vacancies during the period of the initial, slow reaction. Subsequently, the centres of decomposed material grow and the decomposition spikes create strain sufficient to ultimately fracture the crystal, thus creating new reactive surfaces, after which the reaction proceeds in an acceleratory manner. No such mechanism can be envisaged for liquid-phase decompositions. Since a liquid phase is formed [5] in the initial stage of decomposition of $Pb(NO_3)_2$, this mechanism cannot hold good. Therefore, it is assumed that the NO_2^- formed under irradiation catalyses the decomposition. As a result, the rate constants of both the acceleratory and decay stages are enhanced as in the influence of irradiation on solid decomposition.

The catalysing action of NO_2^- has been explained as follows [16]: NO_2^- may act as an electron donor and attract oxygen atoms from the neighbouring nitrate ion. The resulting nitrate ion being oxygen deficient, may attract oxygen atoms from the neighbouring nitrate ions. In this manner the reaction may proceed through the liquid phase and a stream of oxygen would flow from the interior to the surface along a line of NO_2^- ions.

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