

EVALUATION OF KINETIC PARAMETERS FOR THE THERMAL DECOMPOSITION OF GAMMA-IRRADIATED STRONTIUM NITRATE BY DYNAMIC THERMOGRAVIMETRY

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(Received 27 February 1984)

ABSTRACT

The thermal decomposition of γ -irradiated strontium nitrate was studied by thermogravimetry (non-isothermal conditions, constant heating rate of 4° min^{-1}). The reaction order, activation energy, frequency factor and entropy of activation were computed by means of the Coats–Redfern, Freeman–Carroll and Horowitz–Metzger methods. The values of E , Z and ΔS obtained by the three methods agree well. The mechanism for the decomposition follows the Mampel model equation, viz., $-\ln(1-\alpha)$ for $g(\alpha)$ and the rate-controlling process is random nucleation with the formation of a nucleus on every particle.

INTRODUCTION

The influence of γ -irradiation on the kinetics of the thermal decomposition of strontium nitrate has been studied [1] over the temperature range 580 – 625° C by the gas evolution method. It has been observed that irradiation increases the initial gas evolution and shortens the induction period. It also enhances the rate constants in the acceleratory and decay stages. This paper reports studies on the thermal decomposition of γ -irradiated strontium nitrate by thermogravimetry (TG) and the evaluation of the kinetic parameters for the decomposition reaction.

There are several methods for the evaluation of the kinetic parameters using TG. Both isothermal and non-isothermal (dynamic) methods [2] may be used, the latter having certain advantages. As pointed out by Doyle [3], one mass-loss curve is equivalent to a large number of isothermal mass-loss curves and a large amount of information is gained without sample-to-sample error, since the same sample is used throughout. Moreover, it is possible to identify the different reaction stages in the system and the kinetics can be calculated over an entire temperature range in a continuous manner [4]. In the non-isothermal method one determination per sample is sufficient. The non-isothermal method was used in the present studies. It appears that

dynamic TG studies have not been made so far with irradiated inorganic salts.

EXPERIMENTAL

Material

GR grade strontium nitrate (Merck, 7872) was used in the form of fine powder (200–240 mesh) without further purification. It was dried and stored in vacuo over phosphorus pentoxide.

Irradiation

Portions of the dried material sealed in glass ampoules were irradiated at room temperature with Co-60 γ -rays to different doses between 100 and 400 Mrad at the dose rate of 0.2 Mrad h⁻¹. The irradiated samples were also preserved over phosphorus pentoxide before thermal decomposition studies.

Estimation of damage

The damage nitrite produced by irradiation was estimated spectrophotometrically as reported earlier [5].

Isothermal annealing

Some of the samples of strontium nitrate and the irradiated samples were annealed in air at 300 °C \pm 1 °C in a thermostated electric hot air oven for 100 h. The damage nitrite in the irradiated samples after annealing was also determined.

TG studies

The mass-loss of strontium nitrate in air was measured on a Stanton automatically recording thermobalance model TR-1. The heating rate was 4° min⁻¹ and chart speed was 13 cm h⁻¹. Measurements were also made in argon by passing it at about 100 ml min⁻¹ through a plug in the bottom of a sheath fitted inside the furnace. The samples were taken in tall narrow silica crucibles to avoid loss by spattering. In all experiments 100 mg of strontium nitrate was used. The recorded total mass-loss in all cases was 51 \pm 1 mg for 100 mg of strontium nitrate. The mass of material remaining after decomposition agreed with the instrument reading.

The thermal decomposition of unirradiated strontium nitrate (sample 1),

the irradiated samples (samples 2–5) and the unirradiated and irradiated samples annealed at 300°C for 100 h (samples 6–10) was studied.

RESULTS

The chemical damage

The relation between the measure of the chemical damage in terms of % NO_2^- induced and the dose of γ -irradiation is given in Fig. 1 (curve A); the chemical damage induced recovered on annealing the irradiated salts. The fraction annealed [5] at 300°C during different time intervals from 0–100 h in the case of strontium nitrate irradiated to 400 Mrad Co-60 γ -rays are also shown in Fig. 1 (curve B).

TG traces

The recorded TG traces were redrawn, using standard curve sets, as mass vs. temperature (TG) curves and are presented in Fig. 2. All TG curves are essentially of the same pattern. In the irradiated samples the decomposition proceeds faster (curves 2–5) while that in the annealed samples (curves 6–10)

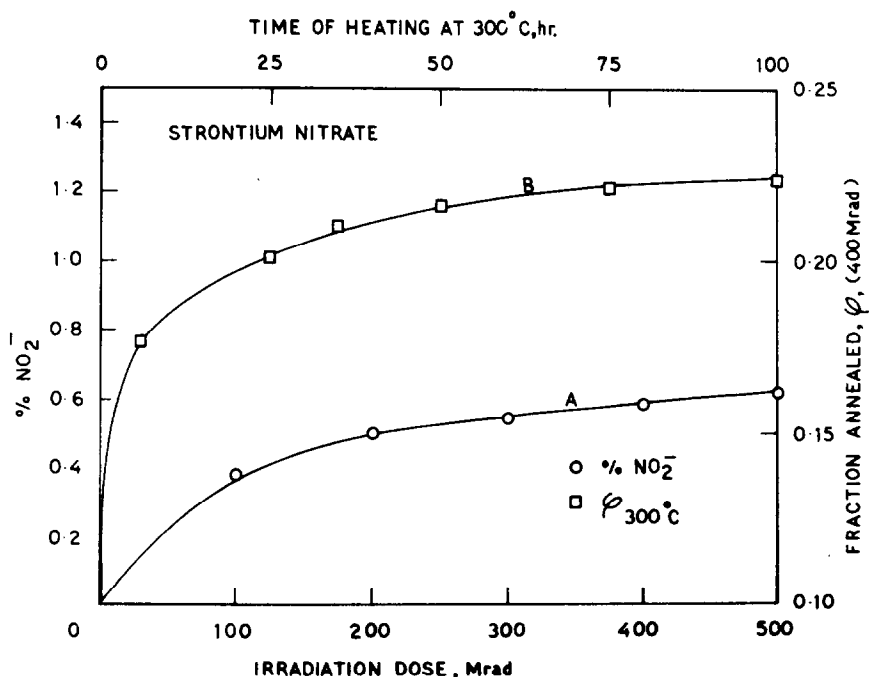


Fig. 1. The dependence of chemical damage in strontium nitrate on the irradiation dose and the time dependence on annealing.

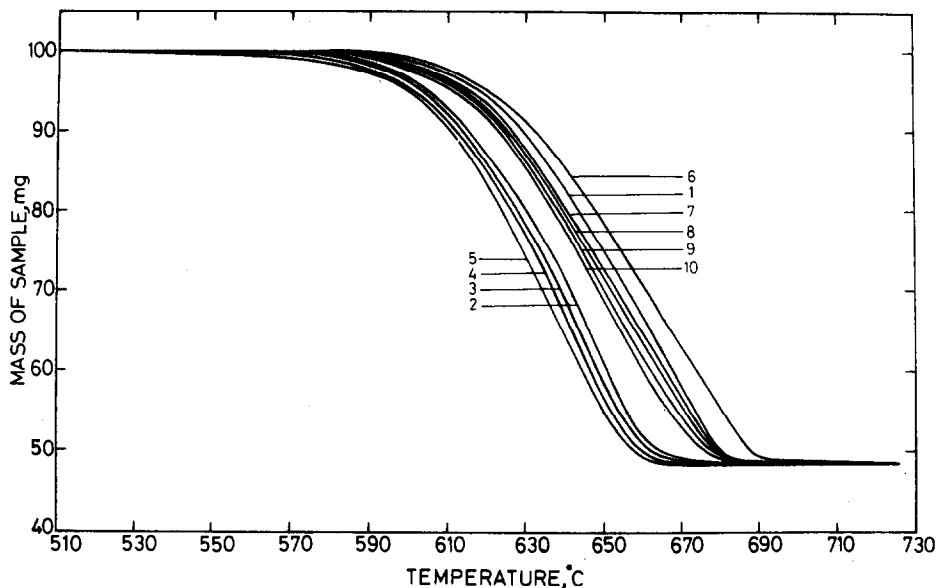


Fig. 2. TG curves of strontium nitrate: (1) unirradiated; (2) irradiated 100 Mrad; (3) irradiated 200 Mrad; (4) irradiated 300 Mrad; (5) irradiated 400 Mrad; (6) unirradiated, annealed for 100 h at 300 °C; (7) irradiated 100 Mrad and annealed; (8) irradiated 200 Mrad and annealed; (9) irradiated 300 Mrad and annealed; (10) irradiated 400 Mrad and annealed.

is slower. Replacement of air by argon had no effect, as shown by the TG curves. These curves are not given in the figure. Three non-isothermal runs were taken for each sample and the mass-loss-temperature relationship was found to be in good agreement in the three runs.

Evaluation of the kinetic parameters

TG may be used to evaluate the kinetic parameters of a solid-state reaction only when the sample changes in mass during a chemical reaction (absorption or elimination of volatile components). The thermal decomposition of strontium nitrate is a solid thermal decomposition, with the elimination of a volatile compound (NO_2) according to reaction (1)



The sample mass decreases and the mass-loss increases with the rise in temperature. The present paper applies the Coats-Redfern [6], Freeman-Carroll [7] and Horowitz-Metzger [8] methods, which use TG curves obtained under the conditions of non-isothermal decomposition, for the evaluation of the kinetic parameters. The methods of calculation based on the three different equations are summarized below.

The Coats-Redfern method [6]

This method considers that in reaction (1) the rate of disappearance of A may be expressed by

$$d\alpha/dt = k(1 - \alpha)^n \quad (2)$$

where α is the fraction of A decomposed at time t ($\alpha = w/w_c$, w is the mass loss at time t , w_c is the maximum mass loss), n is the order of reaction, and k is the rate constant given by

$$k = Z \exp(-E/RT) \quad (3)$$

where Z is the frequency factor (statistical or pre-exponential factor, min^{-1}), E is the activation energy of the reaction, R is the gas constant, and T is the absolute temperature of reaction. At a constant heating rate, ϕ (K min^{-1})

$$\phi = dT/dt \quad (4)$$

By combining eqns. (2), (3) and (4), rearranging and integrating, we obtain

$$\int_0^\alpha d\alpha/(1 - \alpha)^n = Z/\phi \int_0^T \exp(-E/RT) dT \quad (5)$$

The left-hand side of eqn. (5) has two different solutions, depending on the value of n , namely

$$1 - (1 - \alpha)^{1-n}/(1 - n)T^2 \quad \text{for } n \neq 1 \quad (6)$$

and

$$-\log(1 - \alpha)/T^2 \quad \text{for } n = 1 \quad (7)$$

In both cases, the right-hand side of eqn. (5) has the solution

$$ZRT^2/\phi E(1 - 2RT/E) \exp(-E/RT) \quad (8)$$

After taking logarithms, the following equations are obtained

$$\log[1 - (1 - \alpha)^{1-n}/T^2(1 - n)] = \log ZR/\phi E(1 - 2RT/E) - E/2.3RT \quad (9)$$

for $n \neq 1$

and

$$\log[-\log(1 - \alpha)/T^2] = \log ZR/\phi E(1 - 2RT/E) - E/2.3RT \quad \text{for } n = 1 \quad (10)$$

In thermal decomposition reactions such as (1) $\log ZR/\phi E(1 - 2RT/E)$ is practically constant, and plots of

$$\log[1 - (1 - \alpha)^{1-n}/T^2(1 - n)] \text{ vs. } 1/T \quad \text{for } n \neq 1 \quad (11)$$

and

$$\log[-\log(1 - \alpha)/T^2] \text{ vs. } 1/T \quad \text{for } n = 1 \quad (12)$$

respectively, result in a straight line with a slope of $-E/2.3R$ for the

correctly chosen value of n . Thus, using $n = 0$, $1/2$ and $2/3$ in expression (11), and $n = 1$ in expression (12), one can observe for which value of n a straight line results, the reaction order is then easily estimated. E and Z are calculated from the slope and intercept, respectively.

The application of eqns. (11) and (12) to our data on strontium nitrate by the least-squares linear regression method revealed that the best correlation (0.992) is obtained with eqn. (12) and, hence, the order of the reaction is 1 in both the unirradiated and irradiated samples.

For a first-order process the Coats–Redfern equation may be written in the form

$$\log[\ln(w_c/w_c - w)/T^2] = \log ZR/\phi E(1 - 2RT/E) - E/2.3RT \quad (13)$$

where w_c is the maximum mass loss, and w is the total loss in mass up to time t . Since $1 - 2RT/E \approx 1$, a plot of the left-hand side of eqn. (13) against $1/T$ will be linear and E and Z can be calculated from the slope and intercept, respectively.

The energy of activation, E , obtained for different samples of strontium nitrate (untreated, irradiated and annealed samples), the frequency factor, Z , and the entropy of activation, ΔS , are given in Table 1. The entropy of activation was obtained from the equation

$$Z = (kT_s/h) \exp(\Delta S/R) \quad (14)$$

where k is the Boltzman constant, h is Planck's constant and T_s is the peak temperature of decomposition.

The Freeman–Carrol method [7]

The Freeman–Carrol equation was used in the form

$$\Delta \log(dw/dt)/\Delta \log w_r = (-E/2.3 R) \Delta(1/T)/\Delta \log w_r + n \quad (15)$$

where $w_r = w_c - w$. The temperature slopes dw/dT were converted into time slopes dw/dt using the relation

$$dw/dt = (dw/dT)(dT/dt) = (dw/dT)\phi \quad (16)$$

A plot of $\Delta(1/T)/\Delta \log w_r$ vs. $\Delta \log(dw/dt)/\Delta \log w_r$ was found to be linear indicating that the order of the reaction is unity.

The usual first-order rate law expression

$$dx/dt = k(a - x) \quad (17)$$

can be put in the form

$$dw/dt = kw_r \quad (18)$$

Combining eqn. (18) with the Arrhenius equation, we get

$$\log[(dw/dt)/w_r] = -(E/2.3RT) + \log Z \quad (19)$$

TABLE 1

Kinetic parameters calculated using the Coats-Redfern (CR), the Freeman-Carroll (FC) and the Horowitz-Metzger (HM) equations

Sample Sr(NO ₃) ₂	T _i (°C)	T _f (°C)	T _c (°C)	Kinetic parameters								
				E (kJ mol ⁻¹)			Z (s ⁻¹)			ΔS (J K ⁻¹ mol ⁻¹)		
				CR	FC	HM	CR	FC	HM	CR	FC	HM
1. Unirradiated	590	690	650	424.5	455.9	454.1	1.7 × 10 ²³	1.1 × 10 ²⁵	5.1 × 10 ²³	190.6	225.2	199.6
2. Irrad. 100 Mrad	580	670	642	412.8	431.8	449.1	9.0 × 10 ²²	1.1 × 10 ²⁴	5.9 × 10 ²³	185.2	206.0	200.8
3. Irrad. 200 Mrad	580	670	644	408.5	442.7	441.7	5.6 × 10 ²²	5.8 × 10 ²⁴	3.6 × 10 ²³	181.3	219.8	216.0
4. Irrad. 300 Mrad	570	670	647	391.0	420.8	436.2	6.0 × 10 ²¹	3.3 × 10 ²³	1.4 × 10 ²⁴	162.7	196.1	208.3
5. Irrad. 400 Mrad	560	670	644	369.5	412.0	415.7	3.7 × 10 ²⁰	1.2 × 10 ²³	1.1 × 10 ²³	139.5	187.7	187.1
6. Unirrad., annealed	600	690	648	389.0	340.8	410.4	1.2 × 10 ²¹	1.6 × 10 ¹⁸	4.4 × 10 ²²	149.0	94.4	179.2
7. Irrad. 100 Mrad, annealed	590	680	646	397.5	357.6	426.6	5.3 × 10 ²¹	2.3 × 10 ¹⁹	4.3 × 10 ²³	161.7	116.4	198.2
8. Irrad. 200 Mrad, annealed	590	680	647	394.2	361.9	424.3	3.7 × 10 ²¹	4.4 × 10 ¹⁹	3.0 × 10 ²³	158.6	121.9	195.1
9. Irrad. 300 Mrad, annealed	590	680	650	392.4	368.4	425.3	3.1 × 10 ²¹	1.2 × 10 ²⁰	2.8 × 10 ²³	157.3	130.0	194.7
10. Irrad. 400 Mrad, annealed	580	680	653	392.3	381.6	433.0	3.4 × 10 ²¹	7.3 × 10 ²⁰	6.5 × 10 ²³	157.9	145.1	201.5

A plot of the left-hand side of eqn. (19) against $1/T$ should, therefore, be linear and E and Z can be obtained from the slope and intercept, respectively. The entropy of activation was calculated as before. Table 1 gives the kinetic parameters obtained on analysis of data by the Freeman–Carroll method.

The Horowitz–Metzger method [8]

The Horowitz–Metzger equation applicable to a first-order kinetic process is

$$\log[\log(w_c/w_r)] = E\theta/2.3RT_s^2 - \log 2.3 \quad (20)$$

where $\theta = T - T_s$. A plot of $\log[\log(w_c/w_r)]$ vs. θ should be linear, from the slope of which E can be calculated. The pre-exponential factor, Z , can be calculated from the equation

$$E/RT_s^2 = Z/\theta \exp(-E/RT_s) \quad (21)$$

The entropy of activation was calculated from the equation used earlier for the purpose. The results of the analysis of data by the Horowitz–Metzger method are given in Table 1.

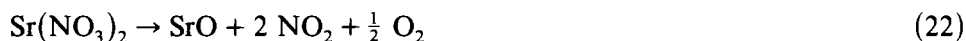
The slopes and intercepts of all the plots obtained by the three methods given above were calculated by the least-squares linear regression method and E and Z values were calculated therefrom. The correlation coefficients, r , were in the range 0.981–0.999. The r values are not given in Table 1. The E and Z values obtained by means of the Coats–Redfern, Freeman–Carroll and Horowitz–Metzger methods show that the agreement between the three methods is quite good (within 10%).

DISCUSSION

Duval [9] and Wendlandt [10] reported that unirradiated strontium nitrate is stable up to 280°C and yields a perfectly horizontal level which starts at room temperature. Decomposition then sets in and proceeds very slowly but becomes explosive above 600°C. The disintegration appears to be complete near 820°C. The succeeding horizontal is due to the oxide SrO. The DTA of strontium nitrate has been reported by Campbell and Gordon [11] who observed fusion at 618°C, evolution of nitrous fumes from 635 to 715°C and vigorous bubbling commencing at 672°C. Using a higher heating rate of 10°C min⁻¹ Campbell et al. [12] found that the actual thermal decomposition accompanied by evolution of nitrous fumes began at 600°C and was complete at 745°C. The end product reported was SrO which is stable up to 1100°C [13].

In the present investigations strontium nitrate melted at 570°C, in agreement with the melting point reported by Mellor [14]. The temperature of

inception of decomposition (T_i) and the temperature of completion (T_f) were found to be 590 and 690 °C, respectively with the peak temperature of decomposition (T_s) at 650 °C. The overall decomposition of the substance occurs as follows



obeying first-order kinetics. Irradiation lowers the value of T_i , T_f and T_s but does not significantly alter the reaction interval ($T_f - T_i$). Annealing of the unirradiated salt for 100 h at 300 °C raises T_i but does not change T_s or T_f . Annealing of the irradiated samples raises T_i and T_f to the values for the unirradiated salt but does not appreciably change T_s (Table 1). The rise in T_i and T_f on annealing is due to the removal of the defects introduced by irradiation. The end product in all cases has been confirmed by X-ray analysis to be SrO.

The values of the activation energy for the decomposition of unirradiated strontium nitrate and strontium nitrate irradiated to 100 and 400 Mrad ^{60}Co γ -rays obtained in earlier studies [1] are 430.5, 418.8 and 368.6 kJ, respectively. These values agree well with those obtained in the present investigations. Table 1 shows that the activation energy decreases only to a small extent with an increase in irradiation dose. The small change upon irradiation suggests that the same chemical processes govern the decomposition of both the unirradiated and the irradiated salt.

The role of irradiation in solid decompositions has been studied extensively [15]. In systems containing molecular ions, irradiation produces chemical damage, displacements and extended lattice defects [16–18]. The influence of irradiation on solid decompositions has been ascribed to these effects which produce as well as facilitate formation and growth of nucleation centres [19]. The relative contribution of crystal defects and chemical damage fragments has, however, not been ascertained. Generally, the effect of irradiation is to decrease the induction period, if any, and decrease the energy of activation of the decomposition. 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 initial period of the reaction. Subsequently, the centres of decomposed material grow and the decomposition spikes create strain sufficient to ultimately fracture the crystals thus creating new reactive surfaces whereafter the reaction proceeds in an accelerating manner. However, such a mechanism cannot be envisaged for decompositions like the present case, because the crystal defects are removed when the irradiated salt melts before decomposition and only the chemical damage persists.

The primary radiolytic fragments produced when ionic nitrates are irradiated with ^{60}Co γ -rays are NO_2^- and O. On radiolysis, decomposition takes place at normal lattice sites and is not primarily associated with the original

lattice defects. The radiolytic oxygen remains trapped in the crystal lattice [18].

The fall in the initial horizontal level in the case of the irradiated samples (Fig. 2 curves 2–5) can be attributed to the effect of irradiation. In the initial stages the concentration of defects and chemical damage is greater and this accelerates the thermal decomposition. However, on melting, a large proportion of the radiolytic oxygen trapped in the crystal lattice escapes and hence the recombination of NO_2^- with O_2 will be small leaving behind a major portion of NO_2^- . This NO_2^- catalyses the decomposition of strontium nitrate. Due to the catalysing effect the activation energy and entropy of activation are lowered. The fact that NO_2^- formed under irradiation catalyses the decomposition has been confirmed by the thermogravimetric studies [20] of strontium nitrate doped with NO_2^- at millimolar concentrations (10^{-4} – 10^{-1} M).

The values of E , Z and ΔS are constant for the samples annealed before decomposition (Table 1). Preheating of the samples anneals the effects produced by irradiation and hence the constancy in the values of E , Z and ΔS .

Mechanism of reaction from non-isothermal TG traces

Deduction of the mechanism of the reaction by use of non-isothermal kinetic methods has been discussed by Sestak and Berggren [21] and Satava [22]. The procedure used by Satava is based on the assumption that the non-isothermal reaction proceeds in an infinitesimal time interval isothermally, where the rate may be expressed as

$$d\alpha/dt = Z \exp(-E/RT) f(\alpha) \quad (23)$$

where $f(\alpha)$ depends on the mechanism of the process. With a constant temperature increase, $dT/dt = \phi$, integration of eqn. (23) leads [22,23] to

$$\int_0^\alpha d\alpha/f(\alpha) = g(\alpha) = ZE/R\phi p(x) \quad (24)$$

where $p(x)$ is defined as [23–26]

$$p(x) = \exp -x/x - \int_{+x}^\alpha (\exp -u/u) du = (\exp -x/x) + E_i(-x) \quad (25)$$

where $u = E/RT$, $x = E/RT_\alpha$ and T_α is the temperature at which the fraction α of the starting material has reacted.

From the logarithmic form of eqn. (24)

$$\log g(\alpha) - \log p(x) = \log ZE/R\phi \quad (26)$$

it can be seen that the right-hand side is independent of the temperature,

while the left-hand side is temperature dependent. To a first approximation, the function $\log p(x)$ is a linear function of $1/T_\alpha$ if x is sufficiently large and, therefore, $\log g(\alpha)$ must also be a linear function of $1/T_\alpha$. For the correct mechanism, $\log g(\alpha)$ vs. $1/T_\alpha$ should be a straight line. For other incorrect mechanisms, this will not be true. Although the sensitivity of this procedure for mechanism determination is not very high, it yields very useful information.

The types of mechanisms most frequently encountered are shown in Table 2, while Table 3 illustrates the computational approach to obtain E and Z for the series of samples of strontium nitrate studied, citing unirradiated strontium nitrate as an example. The functional values of $g(\alpha)$ were obtained using the table of Sharp et al. [27] and E from the slope was calculated by the method of Sestak [28]. For nearly the same value of r , the operating mechanism is chosen by comparing the E values with those obtained by nonmechanistic equation. It is found that the F_1 mechanism gives the maximum correlation in all cases (Table 4).

Analysis of data presented in Table 4 shows that the mechanism for the decomposition of strontium nitrate, both unirradiated and irradiated, follows the Mampel model equation [29], viz., $-\ln(1 - \alpha)$ for $g(\alpha)$ and the rate-controlling process is random nucleation with the formation of a nucleus on every particle. The agreement of the values of E and Z obtained by the mechanistic equation (Table 4) with those from the non-mechanistic equations (Table 1) confirms the mechanism suggested above.

TABLE 2

Mechanistic equations

Function	Equation	Rate-controlling process
D_1	$\alpha^2 = kt$	One-dimensional diffusion
D_2	$(1 - \alpha) \ln(1 - \alpha) + \alpha = kt$	Two-dimensional diffusion, cylindrical symmetry
D_3	$[1 - (1 - \alpha)^{1/3}]^2 = kt$	Three-dimensional diffusion, spherical symmetry; Jander equation
D_4	$(1 - 2/3\alpha) - (1 - \alpha)^{2/3} = kt$	Three-dimensional diffusion, spherical symmetry; Ginstling-Brounshtein equation
F_1	$-\ln(1 - \alpha) = kt$	Random nucleation, one nucleus on each particle; Mampel equation
A_2	$[-\ln(1 - \alpha)]^{1/2} = kt$	Random nucleation, Avrami equation I
A_3	$[-\ln(1 - \alpha)]^{1/3} = kt$	Random nucleation, Avrami equation II
R_2	$1 - (1 - \alpha)^{1/2} = kt$	Phase boundary reaction, cylindrical symmetry
R_3	$(1 - (1 - \alpha)^{1/3}) = kt$	Phase boundary reaction, spherical symmetry

TABLE 3
 Computation of E and Z using mechanism-based equations for unirradiated strontium nitrate

Temperature	$1/T(K) \times 10^3$	α	$\ln g(\alpha)$ for the mechanism											
			D_1	D_2	D_3	D_4	F_1	R_2	R_3	A_2	A_3			
590	1.1587	0.01	-9.2103	-9.2103	0.0000	0.0000	-4.5952	-5.2983	-5.7138	-2.2996	-1.5334			
600	1.1455	0.03	-7.0131	-7.6009	-9.2103	-9.2103	-3.4900	-4.1931	-4.5952	-1.7458	-1.1638			
610	1.1325	0.06	-5.6268	-6.3200	-7.8240	-7.8240	-2.7822	-3.4900	-3.8922	-1.3915	-0.9276			
620	1.1198	0.11	-4.4145	-5.0672	-6.5023	-6.5713	-2.1499	-2.8717	-3.2675	-1.0747	-0.7166			
630	1.1074	0.21	-3.1213	-3.7381	-5.1673	-5.2214	-1.4452	-2.1964	-2.5823	-0.7226	-0.4818			
640	1.0953	0.35	-2.0996	-2.6593	-4.0230	-4.1116	-0.8421	-1.6409	-2.0114	-0.4211	-0.2808			
650	1.0834	0.50	-1.3863	-1.8747	-3.1559	-3.3050	-0.3666	-1.2279	-1.5784	-0.1832	-0.1222			
660	1.0718	0.65	-0.8616	-1.2637	-2.4369	-2.6593	-0.0486	-0.8955	-1.2198	-0.0243	-0.0162			
670	1.0604	0.82	-0.3969	-0.6708,	-1.6628	-2.0062	-0.5393	-0.5522	-0.8315	-0.2696	-0.0797			
680	1.0493	0.99	-0.0201	-0.0577	-0.4853	-1.2255	-1.5272	-0.1054	-0.2426	-0.7636	-0.5092			
Slope			-73.16096	-78.75490	-88.25993	-82.25727	-49.24468	-41.83500	-44.03240	-24.62782	-16.00541			
Intercept			77.42466	83.07736	92.24987	85.48459	52.98417	43.94955	46.01959	26.4799	17.20133			
r			0.98139	0.98958	0.99178	0.99178	0.99647	0.99329	0.99586	0.99641	0.99132			

TABLE 4

Kinetic parameters calculated using the mechanism-based equation, $-\ln(1 - \alpha) = kt$

	Sr(NO ₃) ₂ irradiated to				Sr(NO ₃) ₂ annealed for 100 h at 300 °C					
	100 Mrad	200 Mrad	300 Mrad	400 Mrad	100 Mrad	200 Mrad	300 Mrad	400 Mrad		
Slope	-49.24468	-48.36160	-47.71999	-48.92646	-49.33737	-40.70224	-45.41334	-45.50498	-45.1249	-45.60431
Intercept	52.98417	52.85922	52.29560	53.71637	54.29257	43.45608	48.88605	49.05620	48.72408	49.31822
<i>r</i>	0.99647	0.99790	0.99165	0.99861	0.99775	0.99618	0.99737	0.99736	0.99768	0.99915
<i>E</i> (kJ mol ⁻¹)	424.2	416.7	411.2	421.5	424.9	353.1	392.2	393.0	389.9	393.9
<i>Z</i> (s ⁻¹)	1.0 × 10 ²³	9.0 × 10 ²¹	5.1 × 10 ²²	2.1 × 10 ²³	3.7 × 10 ²³	7.4 × 10 ²⁸	1.7 × 10 ²¹	2.0 × 10 ²¹	1.4 × 10 ²¹	2.6 × 10 ²¹

ACKNOWLEDGEMENT

Grateful thanks of the authors are due to M/s Western India Plywoods, Baliapattam, Kerala, for the irradiations.

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