



Evaluation of Kinetic Parameters for the Thermal Decomposition of γ -Irradiated Anhydrous Calcium Nitrate

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The thermal decomposition of γ -irradiated anhydrous calcium nitrate was studied by dynamic thermogravimetry. The decomposition proceeds in a single stage. The reaction order, activation energy, frequency factor and entropy of activation were calculated using the Coats-Redfern, Freeman-Carroll and Horowitz-Metzger methods and were compared with those of unirradiated anhydrous calcium nitrate. Irradiation enhances the decomposition and the effect increases with the irradiation dose. The activation energy decreases on irradiation. The mechanism of the decomposition of unirradiated and irradiated anhydrous calcium nitrate follows the Mampel model equation, $-\ln(1-\alpha)$ for $g(\alpha)$ and the rate controlling process is random nucleation with the formation of a nucleus on every particle.

Key Words: Calcium nitrate, γ -Rays, Irradiation, Thermal decomposition.

INTRODUCTION

Radiolysis of crystalline alkali and alkaline earth-metal nitrates by ^{60}Co γ -rays has been extensively investigated¹⁻⁵, but little work has been done concerning the effect of irradiation on the kinetics of decomposition of these substances. Pre-exposure to γ -rays is known to introduce the crystal defects and chemical damages. The metallic nitrates such as $\text{Sr}(\text{NO}_3)_2$ and $\text{La}(\text{NO}_3)_3$ ^{6,7} belong to that class of compounds which decompose entirely in the molten state. In such compounds, owing to the formation of liquid phase before decomposition sets in, the crystal defects such as displacements and extended lattice defects generated by irradiation⁸⁻¹⁰ are removed and only the chemical damage produced has significant role in the thermal decomposition of the irradiated material. On the other hand, anhydrous calcium nitrate in the present investigation begins decomposition before melting and proceeds to completion in the melt phase. Hence, both defect concentrations and chemical damage has considerable effect on the decomposition of the salt. The present paper reports the studies on the thermal decomposition of γ -irradiated anhydrous $\text{Ca}(\text{NO}_3)_2$ by dynamic thermogravimetry. This has been carried out with a view to investigate the effect of γ -irradiation on the thermal decomposition and to examine the mechanism of decomposition of both the unirradiated and the irradiated samples on the basis of the models developed for the decomposition of solids^{11,12}.

EXPERIMENTAL

A.R. grade calcium nitrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was dehydrated by slow heating to constant weight at 475 K in a thermostated electric hot air oven and stored over P_2O_5 in vacuum. The loss of weight on heating agreed with the loss of four molecules of water of crystallization. Due to the highly hygroscopic nature of anhydrous calcium nitrate, it was always handled in a dry box.

Irradiation: Samples sealed in Pyrex glass ampoules were irradiated at room temperature with ^{60}Co γ -rays to various doses between 100 and 300 Mrad at a dose rate of 0.2 Mrad h^{-1} . The irradiated samples were also preserved over P_2O_5 in vacuum before the thermal decomposition studies.

Estimation of the damage: The chemical damage induced on irradiation was estimated spectrophotometrically as a function of the concentration of the produced^{13,14} NO_2^- using Systronics spectrophotometer model 105 instrument with an accuracy of $\pm 5 \text{ ppm NO}_2^-$.

Thermogravimetric studies: The mass loss of anhydrous calcium nitrate was measured by Mettler Toledo TGA/SDTA 851° module apparatus at a heating rate of 10 K min^{-1} in nitrogen atmosphere. In all experiments 10 mg of the sample was taken. The recorded mass loss in all cases was $6.59 \pm 0.05 \text{ mg}$, confirming the complete conversion of calcium nitrate to calcium oxide. The mass of materials left behind after decomposition agreed with the instrument reading. All the data have been normalized to an initial mass of 100 mg.

The thermal decomposition of unirradiated calcium nitrate (sample 1) and the irradiated samples (samples 2-4) and the sample irradiated to 100 Mrad and partially annealed at 550 K for 100 h (sample 5) were studied.

RESULTS AND DISCUSSION

Chemical damage: The irradiation by ^{60}Co γ -rays produced chemical damage and other associated lattice defects in anhydrous $\text{Ca}(\text{NO}_3)_2$ crystals as reported earlier for other systems^{15,16}. The concentration of radiolytic products expressed as damage nitrite ions generated in calcium nitrate by various doses of ^{60}Co γ -rays are given in Table-1.

Irradiation dose (Mrad)	100	200	300
NO_2^- (ppm)	3746	4955	5985

Thermogravimetric traces: The recorded TG curves were redrawn, using standard curve sets as percentage mass *versus* temperature (TG) curves and are presented in Fig. 1. All the TG curves are essentially of the same pattern. In the irradiated samples the decomposition proceeds faster (curves 2-4). Replacement of nitrogen by air had no effect on the thermal decomposition and these TG curves are not included in Fig. 1. Three replicate non-isothermal runs were taken for each sample and the mass-loss temperature relationship was found to be in good agreement in all the runs.

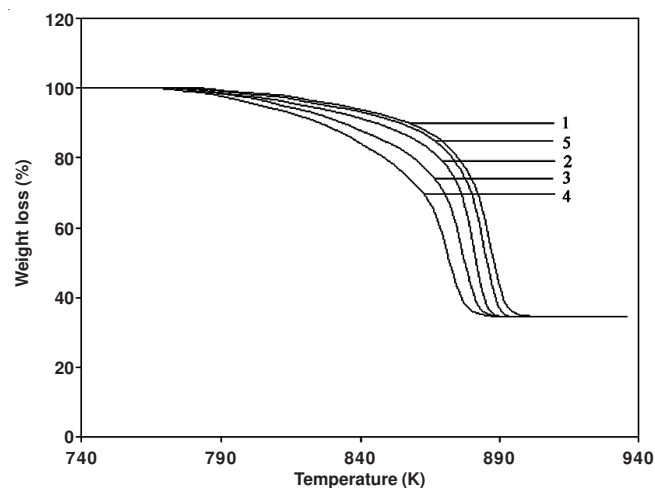


Fig. 1. TG curves of calcium nitrate: 1 - Unirradiated; 2 - Irradiated 100 Mrad; 3 - Irradiated 200 Mrad; 4 - Irradiated 300 Mrad; 5 - Irradiated 100 Mrad and annealed

Effect of partial pre-annealing: The partial pre-annealing of all irradiated samples at 550 K for 100 h reverts back the TG curve pattern very close to the TG curve of unirradiated sample. As a representative, we show the TG curve irradiated to 100 Mrad, partially pre-annealed at the above mentioned temperature and duration (sample 5) in Fig. 1. The initial damage of 3746 ppm of NO_2^- observed for the sample irradiated to 100 Mrad, is reduced to 139 ppm on annealing. This clearly indicates that the recovery of damage in this system is almost

complete on annealing. The decomposition proceeds slower in this sample (curve 5).

Evaluation of the kinetic parameters: The TG curves obtained under conditions of non-isothermal decompositions were used to evaluate the kinetic parameters for the decomposition of calcium nitrate using the Coats-Redfern¹⁷, Freeman-Carroll¹⁸ and Horowitz-Metzger methods¹⁹. The details of calculation have already been described²⁰. The order of the reaction was determined as described previously²⁰ using the Coats-Redfern method¹⁷ from the plots of

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

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

where α is the fraction decomposed, n is the order of the reaction and T is the temperature in K. The application of the eqns. 1 and 2 to present data on calcium nitrate using the least square linear regression method revealed that best correlations is obtained with eqn. 1. Therefore the order of the reaction is unity in both the irradiated and unirradiated samples. The activation energy E and the frequency factor Z were calculated from the slopes and intercepts of the plots respectively. The entropy of activation ΔS was also calculated as shown previously²⁰. The values of E , Z , ΔS and correlation coefficient r are given in Table-2.

The Freeman-Carroll equation¹⁸ was used in the form applicable to a first order process²⁰ and the values of E , Z , ΔS and r are given in Table-2.

The results of the analysis of the present data using the Horowitz-Metzger equation¹⁹ as described earlier²⁰ are also presented in Table-2.

The values of E and Z obtained by these equations are in good agreement.

Chemistry of decomposition: Duval²¹ reported that $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ dehydrates smoothly up to 433 K and the horizontal of the anhydrous salt extends as far as 748 K. Beyond this temperature, reddish vapours are given off.

A recent paper²² reported that the dehydration of $[\text{Ca}(\text{H}_2\text{O})_4](\text{NO}_3)_2$ occurs in two stages to $\text{Ca}(\text{NO}_3)_2$ at 475 K and remains stable up to 775 K. The latter decomposes to CaO at 871 K in a single stage and is connected with the melting of anhydrous $\text{Ca}(\text{NO}_3)_2$ at $T_m = 816$ K. But the temperatures both of the melting (836 K) and of the decomposition (949 K) of $\text{Ca}(\text{NO}_3)_2$ observed by Ettarh and Galway²³ are even a little higher than those determined by previous authors.

In the present investigation, the anhydrous calcium nitrate melted at 820 K which is in good agreement with the melting behaviour reported²². The temperature of inception (T_i) and the temperature completion (T_f) were found to be 792 and 882 K, respectively, with the peak temperature of decomposition (T_p) at 875 K.

$\text{Ca}(\text{NO}_3)_2$ completely decompose to the oxide in accordance with the reaction²³.



obeying first order kinetics. The TG pattern for the decomposition of anhydrous calcium nitrate obtained in the present investigation agreed with the TG pattern for anhydrous portion of $[\text{Ca}(\text{H}_2\text{O})_4](\text{NO}_3)_2$ reported²². Irradiation lowers the T_i , T_f and T_p values (Table-2), but does not alter the reaction interval

(T_f - T_i) significantly. It is interesting to note that most of the alkali and alkaline earth metals generally undergo decomposition in two stages to metallic oxide through the formation of an intermediate nitrite whereas decomposition of calcium nitrate to calcium oxide is a single stage without any intermediate nitrite.

Mechanism of the radiation enhancement of thermal decomposition: In systems containing molecular ions, irradiation produces chemical damage, displacements and extended lattice defects⁸⁻¹⁰. The influence of irradiation on solid decompositions has been ascribed to these effects which produce as well as facilitate formation and growth of nucleation centres²⁴. But the relative contribution of the crystal defects and chemical damage fragment 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. In the present case, the decomposition of calcium nitrate sets in before melting and proceeds to completion in the melt phase. Therefore, both crystal defects and chemical damage produced by irradiation influences the decomposition of the salt. On melting, the lattice defects are removed and only the chemical damage persists. In the melt phase the large proportion of the damage oxygen escapes leaving behind a portion of NO_2^- . The NO_2^- which remains unannealed catalyzes the decomposition. The catalyzing effect of NO_2^- on the thermal decomposition of metallic nitrates has been established earlier²⁴. Owing to the catalyzing effects, activation energy and entropy of activation are lowered.

Preheating of the irradiated samples anneals the effect produced by irradiation and values of E, Z and ΔS reverts back close to the value of the unirradiated $\text{Ca}(\text{NO}_3)_2$ as has been revealed from the TG curves (Fig. 1). The values of kinetic parameters for the sample annealed before decomposition (sample 5) are given in Table-2.

Mechanism of the reaction from non-isothermal TG traces: The non-isothermal kinetic methods discussed by Sestack and Berggren¹¹ and Satava¹², have been used for deducing the mechanism of the thermal decomposition of $\text{Ca}(\text{NO}_3)_2$. The computational approach to obtain the correct mechanism and the corresponding E and Z values has already been discussed²⁰. For the correct mechanism, $\ln g(\alpha)$ versus $1/T$ should be a straight line. The functional values of $\ln g(\alpha)$ required for this purpose were taken from the table of Nair and James²⁵ and E was calculated by the method of Sestak²⁶ from the slope. For almost the same value of r, the operating mechanism was chosen by comparing the E values with those obtained by the non-mechanistic equation. It was found that the F_1 mechanism gives the maximum correlation. Therefore, the decomposition of $\text{Ca}(\text{NO}_3)_2$, both unirradiated and irradiated, follows the Mampel model equation²⁶, 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 in Table-3 with those from the non-mechanistic equation in Table-2 confirms the mechanism suggested.

Conclusion

In the present investigation, the decomposition of calcium nitrate, both unirradiated and irradiated occurs in a single stage without the formation of any intermediate nitrite. It is interesting to note that the decomposition of all samples obey first order kinetics and F_1 mechanism. The activation energy values calculated for both unirradiated and irradiated $\text{Ca}(\text{NO}_3)_2$ suggest that the irradiation enhances the decomposition. The enhancement of decomposition of calcium nitrate is due to the presence of crystal defects and the catalyzing effect of the fragments produced by irradiation.

TABLE-2
KINETIC PARAMETERS FOR THE DECOMPOSITION OF ANHYDROUS IRRADIATED CALCIUM NITRATE

Irradiation dose (Mrad)	T_i (K)	T_f (K)	T_p (K)	Kinetic parameters											
				Coats- Redfern equations				Freeman-Carroll equations				Horowitz-Metzger equations			
				E (kJ mol ⁻¹)	Z (s ⁻¹)	ΔS (JK ⁻¹ mol ⁻¹)	r	E (kJ mol ⁻¹)	Z (s ⁻¹)	ΔS (JK ⁻¹ mol ⁻¹)	r	E (kJ mol ⁻¹)	Z (s ⁻¹)	ΔS (JK ⁻¹ mol ⁻¹)	r
Unirradiated	792	882	875	236.4	2.35×10^{13}	0.51	0.9903	203.30	1.87×10^{11}	-9.09	0.9609	264.7	1.69×10^{15}	9.01	0.9936
100	786	876	868	227.4	8.15×10^{12}	-1.58	0.9941	197.50	1.01×10^{11}	-10.3	0.9596	263.4	3.02×10^{15}	10.15	0.9948
200	782	872	863	218.9	2.77×10^{12}	-3.71	0.9970	193.10	6.14×10^{10}	-11.2	0.9650	253.8	9.50×10^{14}	7.88	0.9973
300	777	867	859	209.5	8.35×10^{11}	-6.09	0.9980	189.02	3.95×10^{10}	-12.1	0.9413	265.4	6.03×10^{15}	11.56	0.9965
100, annealed	790	880	873	231.2	1.21×10^{13}	-0.79	0.9931	200.30	1.30×10^{11}	-9.81	0.9602	258.5	1.21×10^{15}	8.34	0.9956

TABLE-3
KINETIC PARAMETERS FOR THE DECOMPOSITION OF ANHYDROUS IRRADIATED CALCIUM NITRATE CALCULATED USING THE MECHANISM-BASED EQUATION $-\ln(1-\alpha) = KT$

Parameter	$\text{Ca}(\text{NO}_3)_2$	$\text{Ca}(\text{NO}_3)_2$ irradiated to			$\text{Ca}(\text{NO}_3)_2$ annealed for 100 h at 550 K after irradiation to 100 Mrad
		100 Mrad	200 Mrad	300 Mrad	
Slope	-30.1	-29.1	-27.9	-26.83	-29.47
Intercept	33.62	32.5	31.5	30.36	32.97
r	0.9914	0.9948	0.9973	0.9983	0.9939
E (kJ mol ⁻¹)	234.4	225.4	216.9	207.3	229.4
Z (s ⁻¹)	4.01×10^{14}	1.42×10^{14}	4.95×10^{13}	1.54×10^{13}	2.09×10^{14}

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