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THERMAL DECOMPOSITION OF GAMMA-IRRADIATED CALCIUM BROMATE

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ABSTRACT

The thermal decomposition of γ-irradiated $Ca(BrO_3)_2$ was studied by dynamic thermogravimetry. The reaction order, activation energy, frequency factor and entropy of activation were computed using the Coats–Redfern, Freeman–Carroll and Horowitz–Metzger methods and were compared with those of the unirradiated salt. Irradiation enhances the decomposition and the effect increases with irradiation dose. The activation energy decreases on irradiation. The mechanism for the decomposition of unirradiated and irradiated $Ca(BrO_3)_2$ follows the Avrami model equation, $1-(1-\alpha)^{1/3}=kt$, and the rate-controlling process is a phase boundary reaction assuming spherical symmetry.

INTRODUCTION

The radiolysis of crystalline alkali metal and alkaline earth-metal bromates by ^{60}Co γ-rays has been extensively investigated [1–5] but very little work has been done concerning the effect of irradiation on the kinetics of decomposition of these substances. The effect of γ-irradiation on the thermal decomposition of $KBrO_3$ and $NaBrO_3$ has been reported [6,7] from this laboratory. Both these salts belong to that class of compounds which decompose in the molten state. In such compounds, owing to the formation of the liquid phase before decomposition sets in, the crystal defects, such as displacements and extended lattice defects generated by irradiation [8–10], are removed and, therefore, only the chemical damage produced has any significant role in the thermal decomposition of the irradiated material. However, in the case of substances such as $Ca(BrO_3)_2$ which decompose in the solid state (without melting) both the crystal defects and the chemical damage have a significant role in the thermal decomposition of the irradiated salt. The present paper reports on studies of the thermal decomposition of γ-irradiated $Ca(BrO_3)_2$ by dynamic thermogravimetry carried out to investigate the effect of γ-irradiation on the thermal decomposition and to examine the mechanism of decomposition of both the untreated and irradiated samples on the basis of models developed for the decomposition of

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solids [11,12]. The dynamic thermogravimetric method was employed because of its advantages over the isothermal method [13].

EXPERIMENTAL

Materials

AnalaR grade $NaBrO_3$ (Fluka 71326) was used as the starting material in the preparation of $Ca(BrO_3)_2$. $AgBrO_3$ was prepared from $NaBrO_3$ by adding 25 g of $AgNO_3$ to a hot solution containing the stoichiometric amount of $NaBrO_3$. The precipitated $AgBrO_3$ was washed several times to eliminate any $NaNO_3$. The $AgBrO_3$ was then dried under vacuum at 80 ° C.

The stoichiometric amount of pure anhydrous $CaCl_2$ was added to about 3 g of $AgBrO_3$ dissolved in 500 ml of water. The AgCl was filtered and the large volume was evaporated at 80 ° C under vacuum to about 20 ml. Any excess $AgBrO_3$ precipitated was filtered. The solution was then evaporated to dryness at 80 ° C under vacuum. About three to four grams of $Ca(BrO_3)_2$ was obtained. The sample was recrystallized three times and then tested for the presence of silver ions with HCl, and Ag^+ proved absent.

The recrystallized $Ca(BrO_3)_2$ was analysed for bromate purity by the method of Britton and Britton [14]. An average of three results was taken: the sample was 99.5% pure.

The sample was ground to a fine powder (200–240 mesh) and stored in vacuo over P_2O_5.

Irradiation

Portions of the dried material sealed in glass ampoules were irradiated at room temperature with ^{60}Co γ-rays to different doses between 100 and 300 Mrad at the dose rate of 0.2 Mrad h^{-1}. The irradiated samples were also preserved over P_2O_5 before thermal decomposition studies.

Estimation of damage

The direct bromide and the non-bromate bromine formed on radiolysis were determined micropotentiometrically by the method of Boyd et al. [1]. The results in all cases were reproducible to within $\pm 0.2\%$.

TG studies

The mass loss of $Ca(BrO_3)_2$ in air was measured on a Dupont automatically recording thermal analyser, model 990, with thermogravimeter, model 951. The heating rate was 10 ° C min^{-1}. Measurements were also made in nitrogen flowing at about 50 ml min^{-1}. In all experiments, 10 mg of $Ca(BrO_3)_2$ was used. The recorded total mass loss in all cases was 6.16 ± 0.05 mg, confirming complete conversion of $Ca(BrO_3)_2 \cdot H_2O$ to the bromide. The mass of material left behind after decomposition agreed with the instrument reading.

The thermal decomposition of unirradiated $Ca(BrO_3)_2$ (sample 1) and the irradiated samples (samples 2–4) was studied.

RESULTS

Radiolytic damage

The concentrations of the radiolytic products expressed as direct bromide and non-bromate bromine respectively, generated in $Ca(BrO_3)_2$ by different doses of ^{60}Co γ-rays, are given in Table 1.

TG curves

The recorded TG curves were redrawn as mass versus temperature (TG) curves and are presented in Fig. 1. All TG curves are essentially of the same pattern. In the irradiated samples, the decomposition proceeds faster (curves II–IV). Replacement of air by nitrogen had no effect on the decomposition: these TG curves are not included 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 all three runs. The sample loses water of hydration at 120 ° C.

Evaluation of the kinetic parameters

The TG curves obtained under conditions of non-isothermal decomposition were used to evaluate the kinetic parameters using the Coats–Redfern

TABLE 1

Concentration of radiolytic products in γ-irradiated $Ca(BrO_3)_2$

Sample $Ca(BrO_3)_2$	Direct bromide [(mmol Br^- (mol BrO_3^-)$^{-1}$]	Total non-bromate bromide [a] [mmol Br^- (mol BrO_3^-)$^{-1}$]
Unirradiated	–	–
Irrad. 100 Mrad	8.58	64.22
Irrad. 200 Mrad	17.17	117.74
Irrad. 300 Mrad	26.57	166.98

[a] Non-bromate bromine represents total bromate decomposition, i.e. bromide + species other than bromate formed on radiolysis.

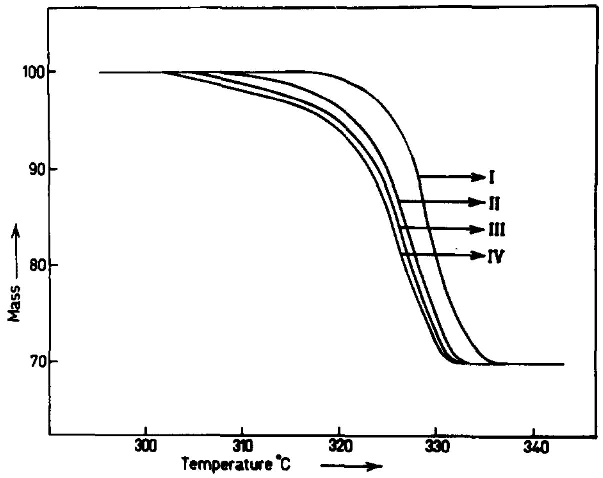

Fig. 1. TG curves of calcium bromate: I, unirradiated; II, irradiated, 100 Mrad; III, irradiated, 200 Mrad; IV, irradiated, 300 Mrad.

[15], Freeman–Carroll [16] and the modified Horowitz–Metzger [17,18] methods. The method of calculation in each case has already been reported [6].

The order of the reaction was determined as described previously [6] using the Coats–Redfern method [15] from the plots of

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

and

$$\log\left[1-(1-\alpha)^{1-n}/T^2(1-n)\right] \quad \text{vs.} \quad 1/T \quad \text{for} \quad n=0,\ \tfrac{1}{2} \text{ or } \tfrac{3}{2} \tag{2}$$

where α is the fraction decomposed, n is the order of the reaction and T is the temperature (in K). The application of eqns. (1) and (2) to our data on

TABLE 2

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

Sample $Ca(BrO_3)_2$	T_i (°C)	T_f (°C)	T_s (°C)	Kinetic parameters			
				CR			
				E (kJ mol^{-1})	Z (s^{-1})	ΔS (J K^{-1} mol^{-1})	r
Unirradiated	320	335	330	997.1	5.6×10^{86}	1408.5	0.9922
Irrad. 100 Mrad	312	332	328	699.0	1.3×10^{61}	917.7	0.9956
Irrad. 200 Mrad	308	332	328	576.6	2.7×10^{50}	713.2	0.9949
Irrad. 300 Mrad	305	332	326	507.0	2.3×10^{44}	597.2	0.9921

$Ca(BrO_3)_2$ using the least-squares linear regression method revealed that the best correlation 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 previously [6]. The values of E, Z and ΔS and the correlation coefficient r are given in Table 2.

The Freeman–Carroll equation [16] was used in the form applicable to a first-order process [6] 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 modified Horowitz–Metzger equation [17,18] as described earlier [6] are also presented in Table 2.

The values of E and Z obtained by the three equations show good agreement, within about 10%.

DISCUSSION

$Ca(BrO_3)_2$ completely decomposes to the bromide in accordance with the reaction [19]

$$Ca(BrO_3)_2 = CaBr_2 + \tfrac{3}{2}O_2 \qquad (3)$$

With more positive alkaline earth metals, the possibility of the bromate decomposing to the oxide and free bromine is less likely [19]. The decomposition of $Ca(BrO_3)_2$ takes place before melting [20]. Bancroft and Gesser [21] observed that the temperature range of decomposition of $Ca(BrO_3)_2$ is 245–270 ° C, the residue consisting of 100% bromide. In the present study the decomposition of unirradiated $Ca(BrO_3)_2$ starts at 320 ° C and was complete at 335 ° C. The residue left consisted of $CaBr_2$ only. Irradiation lowers T_i by 8 ° C in the case of the sample irradiated to 100 Mrad, by 12 ° C

FC				HM			
E (kJ mol^{-1})	Z (s^{-1})	ΔS ($J K^{-1} mol^{-1}$)	r	E (kJ mol^{-1})	Z (s^{-1})	ΔS ($J K^{-1} mol^{-1}$)	r
907.7	1.9×10^{79}	1265.6	0.9858	1013.9	5.6×10^{88}	1446.8	0.9922
707.9	1.8×10^{62}	939.5	0.9647	723.5	4.5×10^{63}	966.5	0.9958
584.2	3.0×10^{51}	733.2	0.9546	602.9	1.2×10^{53}	764.2	0.9955
523.1	1.4×10^{46}	631.5	0.9434	530.8	8.5×10^{46}	646.3	0.9932

in the sample irradiated to 200 Mrad and by 15 ° C in the sample irradiated to 300 Mrad by γ-rays (Table 2). The T_s value for unirradiated $Ca(BrO_3)_2$ is 330 ° C and this is lowered to 326 ° C for the sample irradiated to 300 Mrad. The temperature of completion of the reaction (T_f) is lowered by 3 ° C in the irradiated samples. This is in agreement with the previous observation [6,7] that irradiation lowers T_i, T_s and T_f.

It is evident from Table 2 that the E values decrease with increase in irradiation dose. The activation energy for decomposition of unirradiated $Ca(BrO_3)_2$ obtained in this study (997.1 kJ mol^{-1}) is lower than that obtained (1205 kJ mol^{-1}) by Bancroft and Gesser [21] by about 17%. This difference may be due to the difference in sample size, heating rate or the instrument. The activation energy is lowered on irradiation, by about 30% in the sample irradiated to 100 Mrad, by about 42% in the sample irradiated to 200 Mrad and by about 49% in the sample irradiated to 300 Mrad using γ-rays (Table 2). In the case of $KBrO_3$ and $NaBrO_3$, the activation energy on irradiation did not change to this extent [6,7].

Mechanism of enhancement of thermal decomposition by irradiation

The radiolysis of crystalline alkali and alkaline earth-metal bromates [1–5] yields bromite, hypobromite, bromide and oxygen gas in amounts which vary with the cation in the salt and with the total dose absorbed. On heating the irradiated samples various reactions of the fragments take place. According to Boyd et al. [1] the fragments recombine to form BrO_3^- and Br^-. Hence the concentration of Br^- increases in the irradiated samples on heating. The formation of the bromide in the irradiated samples from the damage fragments allows the formation of the eutectic between the bromate and bromide [22] to proceed with greater ease than that in the unirradiated sample and, hence, decomposition in the irradiated samples is enhanced and the energy of activation is lowered.

In systems containing molecular ions, irradiation produces, in addition to chemical damage, displacements and extended lattice defects [8–10]. The influence of irradiation on solid decomposition has been ascribed to these effects which produce as well as facilitate formation and growth of nucleation centres [23]. The lattice defects introduced in crystals on irradiation are removed when crystal melting takes place [24]. As $KBrO_3$ and $NaBrO_3$ decompose after melting, the lattice defects introduced by irradiation do not have any significant role in the decomposition of these salts. The enhancement of thermal decomposition is entirely due to the chemical damage fragments [6,7]. However, in the case of $Ca(BrO_3)_2$, the lattice defects induced by irradiation do not disappear as the salt does not melt before decomposition and hence enhance the decomposition. The effect observed is due to the chemical damage fragments, to displacements and to the extended

TABLE 3

Kinetic parameters calculated using the mechanism-based equation, $1-(1-\alpha)^{1/3}=kt$

Parameter	$Ca(BrO_3)_2$	$Ca(BrO_3)_2$ irradiated to		
		100 Mrad	200 Mrad	300 Mrad
Slope	183.6	131.4	108.8	95.7
Intercept	111.7	79.8	66.1	58.2
r	0.9869	0.9956	0.9966	0.9946
E (k J mol^{-1})	944.3	676.9	562.5	496.5
Z (s^{-1})	5.4×10^{79}	1.1×10^{57}	1.7×10^{47}	3.7×10^{41}

lattice defects, and therefore the extent of lowering of activation energy is higher than that observed in $KBrO_3$ and $NaBrO_3$.

Irradiation also lowers ΔS. The decrease in ΔS suggests that the decomposition is catalysed in the irradiated samples as has been observed in the case of $KBrO_3$ and $NaBrO_3$.

Mechanism of reaction from non-isothermal TG curves

The mechanism of the thermal decomposition reaction of $Ca(BrO_3)_2$ was established by following the non-isothermal method discussed by Šesták and Berggren [11] and Satavà [12]. The details regarding the computational approach for obtaining the correct mechanism and the corresponding E and Z values have already been discussed [25]. The functional values of ln $g(\alpha)$ required for this purpose were taken from the table of Nair and James [26] and E was calculated by the method of Šesták [27] from the slope. For almost the same value of r, the operating mechanism was chosen by the non-mechanistic equation. It was found that an R_3 mechanism [11] gives the maximum correlation.

The data presented in Table 3 show that the decomposition of $Ca(BrO_3)_2$, both unirradiated and irradiated, follows the Avrami equation [28], $[1-(1-\alpha)^{1/3}]=kt$, and the rate-controlling process is a phase boundary reaction assuming spherical symmetry [12]. The agreement of the values of E and Z obtained by the mechanistic equation (Table 3) with these by the non-mechanistic equation (Table 2) confirms this mechanism.

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