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THERMAL DECOMPOSITION OF GAMMA-IRRADIATED BARIUM BROMATE

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ABSTRACT

The thermal decomposition of γ-irradiated $Ba(BrO_3)_2$ was studied by dynamic thermogravimetry. The reaction order, activation energy, frequency factor and entropy of activation were determined. Irradiation enhances the decomposition by decreasing the activation energy. The mechanism for decomposition of unirradiated and irradiated $Ba(BrO_3)_2$ 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 effect of γ-irradiation on the thermal decomposition of some mono- and di-valent bromates has been reported from this laboratory [1–5]. All these bromates, except $Ca(BrO_3)_2$, decompose in the molten state. Due to the formation of a liquid phase before decomposition, the crystal defects (such as displacements) and extended lattice defects produced by irradiation in these substances are removed, but the chemical damage produced persists and has a significant role in the thermal decomposition of the material [6,7]. On the other hand, in substances like $Ca(BrO_3)_2$ and $Ba(BrO_3)_2$, which decompose entirely in the solid state [4,8], both crystal defects and chemical damage influence the thermal decomposition of the irradiated salt. The results with $Ca(BrO_3)_2$ have already been reported [4]. The present paper reports studies on the effect of γ-irradiation on the thermal decomposition of $Ba(BrO_3)_2$ by thermogravimetry, a technique which has several advantages over the isothermal method described earlier [1].

EXPERIMENTAL

Materials

AnalaR grade $NaBrO_3$ (Fluka 71326) and $BaCl_2$ (B.D.H.) were used. $Ba(BrO_3)_2 \cdot H_2O$ was prepared by dissolving 100 g of $BaCl_2$ in water and adding the stoichiometric amount of $NaBrO_3$. The precipitated $Ba(BrO_3)_2 \cdot H_2O$ was washed several times to eliminate any NaCl, then analysed for bromate purity by the method of Britton and Britton [9]. By repeated recrystallization 99.5% pure $Ba(BrO_3)_2 \cdot H_2O$ was obtained. The sample in the form of fine powder (200–240 mesh) was 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 various doses between 100 and 500 Mrad at a 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. [10] to an accuracy of $\pm 0.2\%$ for repetitive determinations.

TG studies

Thermograms of both unirradiated and irradiated samples were recorded in air using 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 barium bromate was used and the recorded total mass loss in all cases was 2.77 ± 0.05 mg, confirming complete conversion of barium bromate to the bromide. The mass of material left behind after decomposition agreed with the instrument reading. The thermal decomposition of unirradiated $Ba(BrO_3)_2$ (Sample 1) and the irradiated samples (Samples 2–6) was studied.

RESULTS

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

The recorded TG traces were redrawn as mass vs. 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 2–6). 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

TABLE 1

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

Sample	Direct bromide (mmol Br^- (mol BrO_3^- $)^{-1}$)	Total non-bromate bromide [a] (mmol Br^- (mol BrO_3^- $)^{-1}$)
1 unirradiated	–	–
2 Irrad.; 100 Mrad	15.61	75.92
3 Irrad.; 200 Mrad	31.22	139.20
4 Irrad.; 300 Mrad	48.31	197.42
5 Irrad.; 400 Mrad	61.43	247.41
6 Irrad.; 500 Mrad	83.25	298.67

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

found to be in good agreement in all three runs. The sample loses water of hydration at 170 °C.

The TG curves obtained under conditions of non-isothermal decomposition were used to evaluate the kinetic parameters using the Coats–Redfern [11], Freeman–Carroll [12] and the modified Horowitz–Metzger methods [13,14]. The method of calculation in each case has already been reported [1].

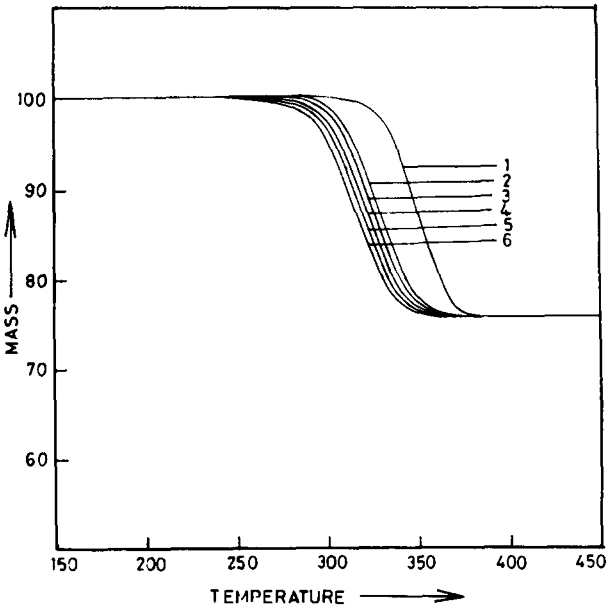

Fig. 1. TG curves of barium bromate: 1, unirradiated; 2, irradiated, 100 Mrad; 3, irradiated, 200 Mrad; 4, irradiated, 300 Mrad; 5, irradiated, 400 Mrad; 6, irradiated, 500 Mrad.

TABLE 2

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

Sample $Ba(BrO_3)_2$	T_i (°C)	T_f (°C)	T_s (°C)	CR			
				E (kJ mol^{-1})	Z (s^{-1})	ΔS (J K^{-1} mol^{-1})	r
Unirradiated	320	375	350	−253.4	4.1×10^{20}	143.7	0.9924
Irrad.; 100 Mrad	300	355	335	−226.9	1.0×10^{19}	113.3	0.9928
Irrad.; 200 Mrad	295	355	330	−217.0	1.6×10^{18}	98.1	0.9962
Irrad.; 300 Mrad	290	355	325	−198.1	4.4×10^{16}	68.0	0.9942
Irrad.; 400 Mrad	285	355	320	−191.4	1.2×10^{16}	57.2	0.9843
Irrad.; 500 Mrad	280	355	315	−178.4	1.0×10^{15}	36.6	0.9736

The order of the reaction was determined as described previously [1] using the Coats–Redfern method [11] from plots of

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

and

$$\log 1-(1-\alpha)^{1-n}/T^2(1-n) \text{ vs. } 1/T \text{ for } n=0,\ 1/2 \text{ or } 3/2 \qquad (2)$$

where α is the fraction decomposed, n is the order of the reaction and T is the temperature (K). The application of eqns. (1) and (2) to our data on $Ba(BrO_3)_2$ 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 unirradiated and irradiated 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 [1]. The values of E, Z and ΔS and the correlation coefficient r are given in Table 2.

The Freeman–Carroll equation [12] was used in the form applicable to a first-order process 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 [13,14] as described earlier [1] are also presented in Table 2.

The values of E and Z obtained by the three equations show good agreement.

DISCUSSION

$Ba(BrO_3)_2 \cdot H_2O$ was converted to the anhydrous salt at 170 °C in agreement with earlier work [15,16]. Barium bromate decomposes to the bromide

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
−260.4	3.7×10^{21}	162.0	0.9925	−277.0	1.4×10^{23}	192.2	0.9904
−238.7	2.7×10^{20}	140.5	0.9784	−240.6	3.7×10^{20}	142.9	0.9910
−206.9	5.2×10^{17}	88.4	0.9944	−228.6	4.8×10^{19}	126.0	0.9944
−181.4	3.3×10^{15}	46.5	0.9962	−216.9	6.4×10^{18}	109.3	0.9927
−172.6	6.3×10^{14}	32.7	0.9954	−200.7	3.3×10^{17}	84.7	0.9808
−161.3	9.5×10^{12}	−2.1	0.9943	−185.8	2.0×10^{16}	61.7	0.9688

in accordance with the reaction

$$Ba(BrO_3)_2 \rightarrow BaBr_2 + 3O_2$$

The decomposition of the unirradiated and the irradiated samples takes place without melting. The decomposition of unirradiated $Ba(BrO_3)_2$ starts at 320 °C and is complete at 375 °C (Table 2). Irradiation lowers the temperature at which decomposition begins (T_i) by 20, 25, 30, 35 and 40 °C in samples irradiated to 100, 200, 300, 400 and 500 Mrads, respectively. Similarly the temperature of completion of decomposition (T_f) and peak temperature (T_s) are also lowered in the irradiated samples, as seen in other systems [1–4].

The activation energy, E, for the decomposition of $Ba(BrO_3)_2$ obtained in the present case (Table 2) is comparable to that obtained by Bancroft and Gesser (217.6 kJ) [17]. The activation energy is lowered on irradiation by about 10, 14, 22, 25 and 30% in samples irradiated to 100, 200, 300, 400 and 500 Mrad γ-rays, respectively (Table 2). The change in activation energy observed in this case is higher than that observed in $KBrO_3$ and $NaBrO_3$ [1–4].

Irradiation also lowers ΔS. The decrease in ΔS suggests that the decomposition is catalyzed in the irradiated samples as reported earlier [1–4].

Radiolysis of crystalline bromates yields bromite, hypobromite, bromide and oxygen gas [10]. When the irradiated samples are heated, various reactions of these fragments take place leading to the formation of BrO_3^- and Br^-. The concentration of Br^- in the irradiated samples thus increases on heating. The Br^- thus formed in the irradiated crystals allows the formation of the eutectic between the bromate and bromide [18] to proceed with greater ease than in the unirradiated sample. The decomposition in the irradiated samples is therefore enhanced and the energy of activation is lowered.

The enhancement of decomposition in the irradiated samples can also be accounted for as follows. It is well known that irradiation produces damage species like hypobromite (OBr^-) and bromite (BrO_2^-) in bromates [10]. The presence of these damage species results in a steady accumulation of strain. At the decomposition temperature this induced strain may rupture the bond, thus creating new reaction surfaces for the decomposition. Also, on irradiation the nuclei already present may grow, resulting in an increase in the thermal decomposition rate.

In systems containing molecular ions, irradiation produces, in addition to chemical damage, displacements and extended lattice defects [6,19,20]. 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 [21]. These lattice defects do not have any significant role in the decomposition of substances that decompose after melting as they are removed when the crystals melt [22]. However, in the case of barium bromate, the lattice defects induced by irradiation do not disappear, since the salt does not melt before decomposition and hence they enhance the decomposition. Therefore the effect observed is due to the chemical damage fragments, to displacements and to the extended lattice defects.

Irradiation also lowers ΔS. The decrease in ΔS suggests that the decomposition is catalyzed in the irradiated samples, as observed in other systems.

Mechanism of reaction from non-isothermal TG traces

The mechanism of the thermal decomposition reaction of $Ba(BrO_3)_2$ was established by following the non-isothermal method discussed by Sestak and Berggren [23] and Satava [24]. 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 Sestak [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 [23] gives the maximum correlation.

The data presented in Table 3 show that the decomposition of $Ba(BrO_3)_2$, 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 [24]. The agreement of the values of E and Z obtained by the mechanistic equation (Table 3) with those from the non-mechanistic equation (Table 2) confirms this mechanism.

TABLE 3

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

Parameter	$Ba(BrO_3)_2$	$Ba(BrO_3)_2$ irradiated to				
		100 Mrad	200 Mrad	300 Mrad	400 Mrad	500 Mrad
Slope	−31.8	−28.0	−26.2	−23.5	−21.5	−20.1
Intercept	49.3	44.7	41.9	37.6	34.3	32.3
r	0.9769	0.9692	0.9757	0.9708	0.9727	0.9601
E (kJ mol^{-1})	−270.1	−238.5	−223.2	−200.4	−183.5	−172.3
Z (s^{-1})	2.5×10^{21}	2.7×10^{19}	1.6×10^{18}	2.1×10^{16}	8.2×10^{14}	1.0×10^{14}

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