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THERMAL DECOMPOSITION OF GAMMA-IRRADIATED POTASSIUM BROMATE BY DYNAMIC THERMOGRAVIMETRY

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ABSTRACT

The thermal decomposition of γ-irradiated $KBrO_3$ was studied by dynamic thermogravimetry. The reaction order, activation energy, frequency factor and entropy of activation were computed by means of the Coats–Redfern, Freeman–Carroll and modified Horowitz–Metzger methods and were compared with those for the unirradiated salt. Irradiation enhances the decomposition and the effect increases with the irradiation dose. The activation energy is decreased on irradiation. The mechanism for the decomposition of unirradiated and irradiated $KBrO_3$ 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

Bromates constitute the largest group of bromine oxysalts. Bancroft and Gesser [1,2] studied the thermal decomposition of several bromates and pointed out that bromates may decompose by two competing reactions

$$MBrO_3 \rightarrow MBr + 3/2\ O_2 \qquad (1)$$

$$MBrO_3 \rightarrow 1/2\ M_2O_2 + 1/2\ Br_2 + 5/4\ O_2 \qquad (2)$$

They used the results of their TGA experiments to calculate the activation energy (E) for the decomposition reactions by the Horowitz–Metzger method [3]. Although the thermal decomposition of bromates has been studied in detail, very little work has been done concerning the effect of irradiation on the kinetics of decomposition of bromates. Jach [4] investigated the thermal decomposition of neutron- and γ-irradiated $KBrO_3$ by the gas evolution method and observed that irradiation increased the rate of decomposition and exerted a marked influence on the Arrhenius plots. The present paper reports studies on thermal decomposition of γ-irradiated $KBrO_3$ by dynamic thermogravimetry, 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 untreated and the irradiated samples on the basis of the models developed for the decomposition of solids [5,6]. Dynamic

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thermogravimetry was employed because of its advantages over the isothermal method [7]. Moreover, very little work appears to have been done on the thermal decomposition of irradiated bromates by dynamic thermogravimetry.

EXPERIMENTAL

Material

GR grade $KBrO_3$ (Merck, 4912) was used in the form of fine powder (200–240 mesh) without furthur purification. It was dried 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 500 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. [8]. The results in all cases were reproducible to within $\pm 0.2\%$.

Isothermal annealing

Some of the samples of $KBrO_3$ and the irradiated samples were annealed in air at $140 \pm 1°C$ in a thermostated electric hot-air oven for 100 h. The damage in the irradiated samples after annealing was also determined.

TG studies

The mass loss of $KBrO_3$ in air was measured on a DuPont automatically recording thermal analyser, model 990 with TG, model 951. The heating rate was 5°C min^{-1}. Measurements were also made in argon flowing at about 100 ml min^{-1}. In all experiments, 30 mg of $KBrO_3$ was used. The recorded total mass loss in all cases was 8.60 ± 0.05 mg, confirming complete conversion to KBr. The mass of material left behind after decomposition agreed with the instrument reading.

The thermal decomposition of unirradiated $KBrO_3$ (sample 1), the irradiated samples (samples 2–5) and the unirradiated and irradiated samples annealed at 140°C for 100 h (samples 6–10) was studied.

TABLE 1

Concentration of radiolytic products in γ-irradiated $KBrO_3$

Sample $KBrO_3$	Direct bromide (mmol Br^-/mol BrO_3^-)	Total non-bromate bromine [a] (mmol Br^-/mol BrO_3^-)
(1) Unirradiated	–	–
(2) Irrad. 100 Mrad	16.39	23.41
(3) Irrad. 200 Mrad	32.78	42.92
(4) Irrad. 300 Mrad	50.73	60.87
(5) Irrad. 500 Mrad	87.41	92.09
(6) Unirrad., annealed	–	–
(7) Irrad. 100 Mrad, annealed	20.14	21.77
(8) Irrad. 200 Mrad, annealed	35.12	39.02
(9) Irrad. 300 Mrad, annealed	54.28	58.92
(10) Irrad. 500 Mrad, annealed	89.75	91.94

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

RESULTS

The chemical damage

The concentrations of the radiolytic products expressed as direct bromide and non-bromate bromine, respectively, generated in $KBrO_3$ by different doses of ^{60}Co γ-rays and the concentration of these species after annealing the samples for 100 h at 140°C are given in Table 1. As can be seen from the table, the concentration of the non-bromate bromine in the irradiated crystals decreases and that of direct bromide increases on annealing.

TG traces

The recorded TG traces 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 2–5). The TG curves of the annealed samples (6–10) fall close to curve 7 and, hence, only curves 6 and 7 are shown in the figure. Replacement of air by argon had no effect on the decomposition, as shown by the TG curves that 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.

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

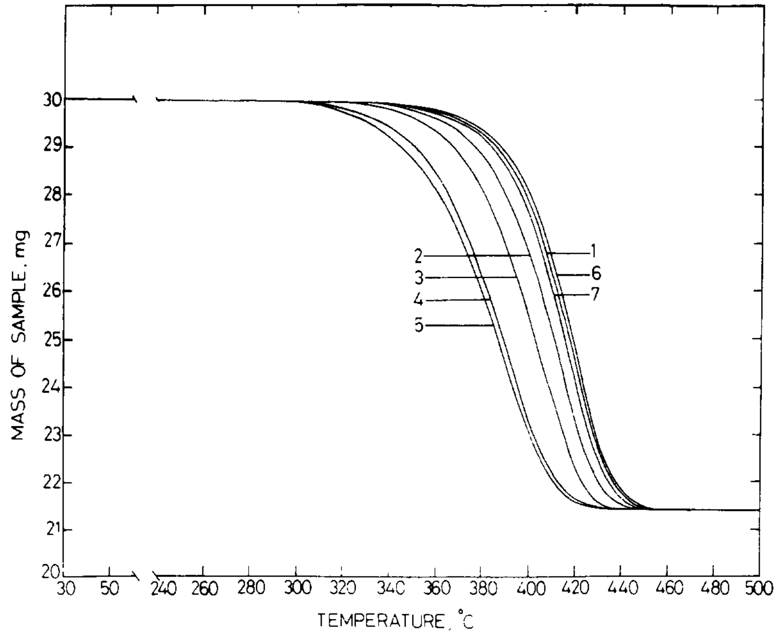

Fig. 1. TG curves of potassium bromate: (1) unirradiated; (2) irradiated 100 Mrad; (3) irradiated 200 Mrad; (4) irradiated 300 Mrad; (5) irradiated 500 Mrad; (6) unirradiated, annealed for 100 h at 140°C; (7) irradiated 100 Mrad and annealed.

[9], Freeman–Carroll [10] and the modified Horowitz-Metzger [3,11] methods. The method of calculation in each case has already been reported [12,13].

The Coats–Redfern method [9]

The order of the reaction was determined as described earlier [12] by the use of the Coats–Redfern equation [9] from the plots of

$$\log\left[-\log(1-\alpha)/T^2\right] \text{versus } 1/T \qquad \text{for } n=1 \tag{3}$$

and

$$\log\left[1-(1-\alpha)^{1-n}/T^2(1-n)\right] \text{versus } 1/T \quad \text{for } n \neq 1 \tag{4}$$

where α is the fraction decomposed, n is the order of the reaction and T is the temperature (K). The application of eqns. (3) and (4) to our data on $KBrO_3$ by the least-squares linear regression method revealed that the best correlation is obtained with eqn. (3) and, hence, the order of the reaction is 1 in both the irradiated and unirradiated samples. The activation energy (E) and the frequency factor (Z) were calculated from the slopes and intercepts, respectively, of the plots. The entropy of activation (ΔS) was calculated as shown previously [12]. The values of E, Z, ΔS and correlation coefficient (r) are given in Table 2.

The Freeman–Carroll method [10]

The Freeman–Carroll equation [10] was used in the form applicable for a first-order process [12]

$$\log(\mathrm{d}w/\mathrm{d}t)/w_r = -(E/2.3RT) + \log Z \tag{5}$$

where

$$\mathrm{d}w/\mathrm{d}t = (\mathrm{d}w/\mathrm{d}T)\phi \tag{6}$$

and

$$w_r = w_c - w \tag{7}$$

in which ϕ is the heating rate (K min^{-1}), w is the mass-loss at time t and w_c is the maximum mass loss. A plot of the left-hand side of eqn. (5) versus $1/T$ was linear as required and E and Z were obtained from the slope and intercept, respectively. ΔS was calculated as before [12]. Table 2 gives the kinetic parameters and correlation coefficient, r, obtained by the Freeman–Carroll method.

The Horowitz–Metzger method

The present data were analysed using the Horowitz–Metzger equation [3] as modified by Dharwadkar and Karakhanavala [11] in the form

$$\log\left[\log(1-\alpha)^{-1}\right] = 100E\theta/2.3\ RT_i^2(T_f - T_i) - \log 2.3 \tag{8}$$

where T_i is the temperature of inception of the reaction, T_f is the temperature of completion of the reaction, θ is the difference between the temperature at the inflection point of the thermogram (T_s) and the temperature under consideration, and R is the gas constant. A plot of the left-hand side of eqn. (8) versus θ was linear as required by the theory and E was calculated from the slope. Z and ΔS were calculated as previously described [12]. The results of analysis are given in Table 2.

The E and Z values obtained by means of the Coats–Redfern, Freeman–Carroll and the modified Horowitz–Metzger methods show that the general agreement between these methods is good, within about 10%. However, ΔS values obtained by the three methods show variation. This is due to the difference in the methods employed to derive ΔS. A comparison of the actual magnitude of ΔS is therefore unimportant; the trend in the change of ΔS alone is important.

DISCUSSION

Although the lowest temperature at which weight loss is observable is reported as 370°C by Bancroft and Gesser [2] and Duval [14], the present

TABLE 2

Kinetic parameters calculated using the Coats–Redfern (CR), the Freeman–Carroll (FC)

Sample $KBrO_3$	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
(1) Unirradiated	340	450	427	225.2	1.2×10^{16}	55.8	0.9996
(2) Irrad. 100 Mrad	320	450	416	208.2	8.6×10^{14}	34.0	0.9999
(3) Irrad. 200 Mrad	320	430	413	191.2	6.1×10^{13}	12.0	0.9999
(4) Irrad. 300 Mrad	310	430	397	167.8	1.6×10^{12}	−17.8	0.9999
(5) Irrad. 500 Mrad	310	420	394	154.0	1.3×10^{11}	−38.5	0.9999
(6) Unirrad., annealed	330	450	425	226.6	1.5×10^{15}	57.5	0.9996
(7) Irrad. 100 Mrad, annealed	330	450	420	223.1	9.4×10^{15}	53.8	0.9998
(8) Irrad. 200 Mrad, annealed	330	450	420	224.1	1.2×10^{16}	56.0	0.9999
(9) Irrad. 300 Mrad, annealed	330	450	418	220.7	6.8×10^{15}	51.2	0.9998
(10) Irrad. 500 Mrad, annealed	330	440	414	215.3	2.9×10^{15}	44.3	0.9977

investigations show that the decomposition of $KBrO_3$ begins at 340°C (Table 2), as has been observed by Jach (342°C) [4]. Irradiation lowers T_i by 20°C in the case of samples irradiated to 100 and 200 Mrad, and by 30°C in samples irradiated with 300 and 500 Mrad γ-rays, respectively. In the case of the annealed samples (7–10), the decomposition begins at 330°C, as seen for the pre-annealed unirradiated $KBrO_3$ (sample 6). This is due to the thermal annealing of the radiolytic products in the irradiated samples. Similarly, T_f and T_s for the irradiated samples are lower than those for unirradiated $KBrO_3$. After post-irradiation thermal annealing, these values revert back to the values for unirradiated $KBrO_3$. Thus, the effect of irradiation is to lower the values of T_i, T_f and T_s, as has been observed in the case of strontium nitrate [12].

The existence of the following fragments in irradiated bromates has been reported [15]: BrO_2^-, BrO^-, Br^- and O; small amounts of BrO_3 and BrO_2; and possibly also some BrO_4. Various reactions of the fragments are possible on heating. Boyd and Larson [16] found that a proportion of the oxidizing fragments, which disappears in thermal annealing, recombines to form BrO_3^- and the remainder yields Br^-. They ascribed the Br^- yield to thermal decomposition of BrO^- and possibly of BrO_2 and BrO_3. However, the fact that mere compression converts the oxidizing fragments into BrO_3^- and Br^- shows that the appearance of Br^- occurs by a mechanism that is not one of thermal decomposition [17]. Khare and Mohanty [15] suggested that the reacting species are BrO_2^- and atomic oxygen, and the annealing reaction consists of the recombination of closely spaced fragments of individual damage events

$$BrO_2^- + O \rightarrow BrO_3^- \qquad (9)$$

and the modified Horowitz–Metzger (HM-M) equations

FC				HM-M			
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
249.0	2.0×10^{18}	98.4	0.9908	236.0	1.2×10^{17}	74.9	0.9983
225.5	1.2×10^{18}	67.1	0.9924	228.2	5.8×10^{16}	69.0	0.9986
196.6	3.5×10^{14}	26.6	0.9888	187.1	4.3×10^{13}	9.1	0.9994
174.4	1.3×10^{13}	−0.7	0.9893	177.1	1.5×10^{13}	0.7	0.9986
157.4	5.8×10^{11}	−26.3	0.9786	151.6	1.5×10^{11}	−37.4	0.9995
254.7	5.4×10^{18}	106.6	0.9884	244.0	5.5×10^{17}	87.6	0.9993
255.0	7.0×10^{18}	108.8	0.9877	234.6	1.4×10^{17}	76.4	0.9992
243.1	8.3×10^{17}	91.1	0.9904	231.5	8.2×10^{16}	71.9	0.9992
255.1	8.5×10^{18}	110.5	0.9846	227.8	4.8×10^{16}	67.4	0.9994
246.5	1.9×10^{18}	98.2	0.9704	225.2	3.8×10^{16}	65.6	0.9983

together with the random recombination of BrO_2^- fragments and O_2 throughout the crystal

$$BrO_2^- + O_2 \rightarrow BrO_3^- + O \tag{10}$$

followed by the rapid reaction

$$BrO^- + O \rightarrow Br^- + O_2 \tag{11}$$

Thus, on thermal annealing, the oxidizing fragments disappear, yielding BrO_3^- and Br^-. Due to thermal annealing of the radiolytic products, the TG curves of $KBrO_3$ samples annealed after irradiation (7–10) fall close to that of the unirradiated salt. The rise in T_i and T_f for samples 7–10 is also due to the removal of damage fragments on thermal annealing.

Bancroft and Gesser [2] calculated the activation energy for the decomposition of $KBrO_3$ using the method of Horowitz and Metzger on the assumption that the reaction is of first order and obtained a value of $E = 493.7$ kJ mol^{-1}. In a later investigation, Joseph and Nair [18] obtained a value of 453.0 kJ. According to Solymosi [19], the reliability of such high values of E is doubtful and these are not suitable even for qualitative comparison. The value of E for the decomposition of unirradiated $KBrO_3$ in the present investigations is 225.2 kJ, which is comparable to the value reported by Jach [4] and also close to the dissociation energy [19] of the Br–O bond (209.2 kJ). Table 2 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.

According to derivatographic studies [20], the decomposition of $KBrO_3$

TABLE 3

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

	$KBrO_3$	$KBrO_3$ irradiated to				$KBrO_3$ annealed for 100 h at 140°C	$KBrO_3$ annealed for 100 h at 140°C after irradiation to			
		100 Mrad	200 Mrad	300 Mrad	500 Mrad		100 Mrad	200 Mrad	300 Mrad	500 Mrad
Slope	−25.71426	−23.72644	−22.93084	−19.57322	−18.30706	−26.24185	−25.51050	−25.42214	−24.95656	−24.90930
Intercept	35.70645	33.14651	32.52963	28.10974	26.32864	36.42507	35.49453	35.42034	34.77532	34.88793
r	0.99610	0.99609	0.99961	0.99778	0.99934	0.99796	0.99747	0.99712	0.99716	0.99738
E (kJ mol^{-1})	224.8	208.1	201.4	173.2	162.6	229.2	223.0	222.3	218.4	217.9
Z (s^{-1})	3.2×10^{15}	2.5×10^{14}	1.3×10^{14}	1.6×10^{12}	2.7×10^{11}	6.6×10^{15}	2.6×10^{15}	2.4×10^{15}	1.3×10^{15}	1.4×10^{15}

begins after melting. Endotherms indicate melting occurring at 380 and 400°C and exotherms relate to decomposition at 400 and 430°C, respectively. Jach [4] has suggested that as a result of the eutectic formed with bromide produced during the decomposition, the bromate melts and, hence, the decomposition occurs partially in the solid and partially in the molten state. The bromide ion also catalyses the decomposition by donating an electron to an oxygen atom of a bromate ion that has still to be decomposed, thereby promoting the splitting of the latter.

The damage fragments formed in $KBrO_3$ upon exposure to γ-rays also constitute decomposition nuclei in the solid. The increase in the rate of decomposition in irradiated $KBrO_3$ may therefore be attributed to the increased concentration of damage fragments. Moreover, KBr formed on irradiation or by the most instantaneous decomposition of the other damage fragments such as BrO^- and BrO_2^- also catalyses the decomposition, and, consequently, the energy of activation for the decomposition of irradiated $KBrO_3$ is decreased.

Irradiation also lowers ΔS (Table 2). The decrease in the entropy of activation for the irradiated samples suggests that the decomposition is catalysed. On annealing, ΔS reverts back to the value for the unirradiated $KBrO_3$.

The effect of partial preannealing of the irradiated samples may be explained as follows: when a solid substance in which physical and chemical damage has been induced by irradiation is heated, the damage tends to recover [21–23]. Thus, on heating irradiated $KBrO_3$ at temperatures at which no gross thermal decomposition occurs, the concentration of the lattice defects and of the chemical damage fragments is diminished, the annealed material decomposes at a rate lower than that of the irradiated and unannealed substance and the activation energy of the irradiated and subsequently annealed samples becomes nearly equal to that of the unirradiated sample.

Mechanism of reaction from non-isothermal TG traces

The non-isothermal kinetic methods discussed by Sestak and Berggren [5] and Satava [6] have been used for deducing the mechanism of decomposition of $KBrO_3$. The computational approach to obtain the correct mechanism and the corresponding E and Z values has already been discussed [12]. 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 these authors [24] and E was calculated by the method of Sestak [25] from the slope. For almost the same value of r, the operating mechanism is chosen by comparing the E values with those obtained by the non-mechanistic equation. It is found that R_3 mechanism [5] gives the maximum correlation in all cases (Table 3).

The data presented in Table 3 show that the decomposition of $KBrO_3$, both unirradiated and irradiated, follows the Avrami equation [26], $[1-(1-\alpha)^{1/3}]=kt$, and the rate-controlling process is a phase boundary reaction assuming spherical symmetry [6]. The agreement of the values of E and Z obtained by the mechanistic equation (Table 3) with those by the non-mechanistic equation (Table 2) confirms this mechanism.

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