EVALUATION OF KINETIC PARAMETERS FOR THE THERMAL DECOMPOSITION OF γ-IRRADIATED SODIUM BROMATE BY DYNAMIC THERMOGRAVIMETRY

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ABSTRACT

The thermal decomposition of γ-irradiated $NaBrO_3$ 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 the irradiation dose. The activation energy decreases on irradiation. The mechanism for the decomposition of unirradiated and irradiated $NaBrO_3$ 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

The effect of γ irradiation on the thermal decomposition of $KBrO_3$ has been reported in a previous publication from this laboratory [1]. The study of $NaBrO_3$ reported in this work is an extension of the above. $NaBrO_3$ decomposes via a mechanism in which the surfaces become completely covered with a layer of product (NaBr) right from the start of the reaction, which then proceeds by an advance of the interface created between the undecomposed bromate and the product bromide [2]. At certain temperatures, the simultaneous presence of these two species allows a type of eutectic to be formed and melting occurs. The presence of the resulting liquid phase then plays a dominant role in the decomposition. Owing to the formation of the liquid phase the crystal defects, such as displacements and extended lattice defects generated by irradiation, are removed and only the chemical damage persists [3,4]. Hence $NaBrO_3$ is a well-suited system for studying the effect of chemical damage produced by irradiation on the thermal decomposition of inorganic salts. Bancroft and Gesser [5] and Jach

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[6] have studied the effect of irradiation on the thermal decomposition of $NaBrO_3$, but a detailed kinetic study was not undertaken by these workers.

This paper reports the results of a study on the thermal decomposition of $NaBrO_3$ by dynamic thermogravimetry. The aims of this work were to investigate the effect of γ irradiation on the thermal decomposition, to evaluate the kinetic parameters 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 [7,8]. The dynamic thermogravimetric method was employed because of its advantages over the isothermal method [9].

EXPERIMENTAL

Material

AnalaR grade $NaBrO_3$ (Fluka 71326) was used in the form of fine powder (200–240 mesh) without further 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 various doses between 100 and 400 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]. The results in all cases were reproducible to within $\pm 0.2\%$.

TG studies

Thermograms of both unirradiated and irradiated samples were recorded in nitrogen using a Du Pont automatically recording thermal analyser model 990 with TG model 951. Dry nitrogen was purged at a rate of 50 cm^3 min^{-1}. The heating rate was 10 °C min^{-1}. In all experiments, 10 mg of $NaBrO_3$ was used. The recorded total mass loss in all cases was 3.19 ± 0.05 mg, confirming the complete conversion to NaBr. The mass of material left behind after decomposition agreed with the instrument reading.

The thermal decomposition of unirradiated $NaBrO_3$ (sample 1) and the irradiated samples (samples 2–4) was studied.

RESULTS

The chemical damage

The concentrations of the radiolytic products (expressed as direct bromide and non-bromate bromine) generated in $NaBrO_3$ by various doses of ^{60}Co γ rays are given in Table 1. As can be seen from the table, the concentrations of direct bromide and total non-bromate bromine increase with the irradiation dose. A comparison of the concentrations of the radiolytic products produced in $NaBrO_3$ with those produced in $KBrO_3$ by the same dose of irradiation [1] shows that $NaBrO_3$ is more susceptible to radiolysis. This is in agreement with the results obtained by Boyd and Larson [11].

TG traces

The recorded TG traces were redrawn as mass vs. temperature (TG) curves and are presented in Fig. 1. The initial mass of the sample in each case is normalized to 100 mg. All TG curves are 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 decomposition. Three non-isothermal runs were taken for each sample and the mass loss–temperature relationship showed good reproducibility.

Computation of the kinetic parameters

The kinetic parameters for the decomposition of $NaBrO_3$ were calculated using the Coats–Redfern [12], Freeman–Carroll [13] and Horowitz–Metzger [14] methods. The method of computation in each case has already been described [1,15].

TABLE 1

Concentration of radiolytic products in γ-irradiated $NaBrO_3$

Sample NaBrO$_3$	Direct bromide (mmol Br$^-$ (mol BrO$_3^-$)$^{-1}$)	Total non-bromate bromine [a] (mmol Br$^-$ (mol BrO$_3$)$^{-1}$)
(1) Unirradiated	–	–
(2) Irrad. 100 Mrad	15.35	25.62
(3) Irrad. 200 Mrad	30.70	46.98
(4) Irrad. 300 Mrad	47.51	66.63
(5) Irrad. 400 Mrad	64.50	83.50

[a] Non-bromate bromine represents total bromate decomposition, i.e. bromide + species other than bromate formed on radiolysis.
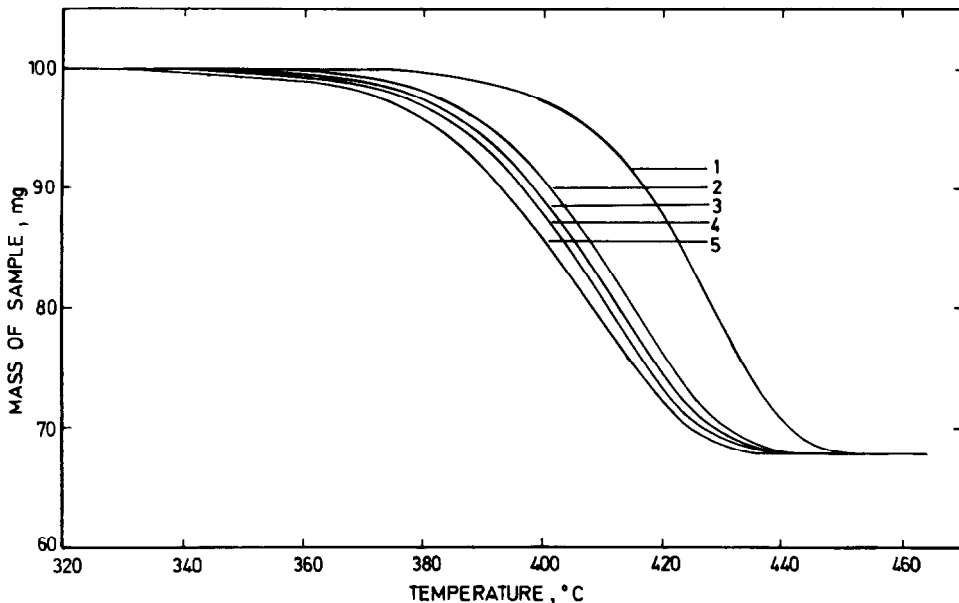
Fig. 1. TG curves of sodium bromate: (1) unirradiated; (2) irradiated, 100 Mrad; (3) irradiated, 200 Mrad; (4) irradiated, 300 Mrad; (5) irradiated, 400 Mrad.

The order of the reaction was determined as described previously [15] using the Coats–Redfern equation [12] from the plots of

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

and

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

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 $NaBrO_3$ 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 respectively of the plots. The entropy of activation ΔS was also calculated as shown previously [15]. The values of E, Z, ΔS and the correlation coefficient r are given in Table 2.

The Freeman–Carroll equation [13] was used in the form applicable to a first-order process [15] and the values of E, Z, ΔS and the correlation coefficient are given in Table 2.

The results of the analysis of the present data using the Horowitz–Metzger equation [14] as described earlier [15] are also presented in Table 2.

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

TABLE 2

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

Sample NaBrO$_3$	T_i (°C)	T_f (°C)	T_s (°C)	Kinetic parameters											
				CR				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	E (kJ mol^{-1})	Z (s^{-1})	ΔS (J K^{-1} mol^{-1})	r
(1) Unirradiated	380	450	427	348.5	3.1×10^{25}	236.1	0.9988	369.4	2.4×10^{27}	272.1	0.9969	380.8	2.5×10^{28}	291.5	0.9975
(2) Irrad. 100 Mrad	360	450	418	320.0	7.5×10^{23}	205.2	0.9882	329.0	7.3×10^{24}	224.1	0.9956	336.6	2.4×10^{25}	234.0	0.9852
(3) Irrad. 200 Mrad	350	440	416	282.7	1.1×10^{23}	151.2	0.9960	293.4	1.6×10^{22}	173.2	0.9990	305.1	1.0×10^{23}	188.8	0.9961
(4) Irrad. 300 Mrad	350	440	408	246.3	1.8×10^{18}	97.9	0.9990	261.5	6.3×10^{19}	127.3	0.9941	272.6	5.8×10^{20}	145.7	0.9972
(5) Irrad. 400 Mrad	340	430	404	231.1	1.5×10^{17}	77.0	0.9965	231.0	2.9×10^{17}	82.7	0.9963	256.4	4.1×10^{19}	123.7	0.9934

DISCUSSION

NaBrO$_3$ decomposes entirely to the bromide [16] in accordance with the reaction

$$NaBrO_3 = NaBr + \tfrac{3}{2}O_2 \tag{3}$$
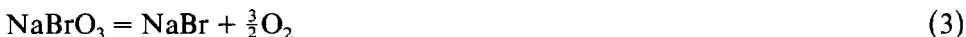
At low pressures the decomposition begins near 320°C [5]. The decomposition kinetics have been studied by Jach [2] in the range 323–430°C. Erdey et al. [17] have shown (using derivatographic studies) that the thermal decomposition of NaBrO$_3$ begins after melting. The endotherm indicates melting at 380°C and the exotherm relates to the decomposition at 400°C. In this study the decomposition of unirradiated NaBrO$_3$ starts at 380°C. Irradiation lowers T_i by 20°C in the case of samples irradiated to 100 Mrad, by 30°C in samples irradiated to 200 and 300 Mrad and by 40°C in samples irradiated to 400 Mrad γ rays (Table 2). The T_s value for unirradiated NaBrO$_3$ is 427°C and this is lowered to 404°C for the sample irradiated to 400 Mrad γ rays. The temperature T_f of completion of reaction is lowered by 20°C in the irradiated samples. Thus, the previous observation that irradiation lowers T_i, T_s and T_f [18] is further confirmed.

It is evident from Table 2 that the E values decrease with an increase in irradiation dose. The activation energy for decomposition of unirradiated NaBrO$_3$ obtained in this study is comparable with that obtained by Bancroft and Gesser [5]. The activation energy is not appreciably changed on irradiation, indicating that the same chemical processes take place in both the unirradiated and irradiated samples. Irradiation also lowers ΔS. The decrease in ΔS suggests that the decomposition is catalysed in the irradiated samples as has been reported in the case of KBrO$_3$ [1].

Mechanism of enhancement of thermal decomposition by irradiation

The radiolysis of crystalline alkali metal bromates with γ rays yields bromite, hypobromite, bromide and oxygen gas in amounts which vary with the alkali metal cation in the salt and with the total dose absorbed [10]. On heating the irradiated samples various reactions of the fragments take place. According to Boyd et al. [10] the fragments recombine to form BrO$_3$$^-$ and Br$^-$. Hence the concentration of Br$^-$ increases in the irradiated samples on heating. The formation of NaBr in the irradiated samples from the damage fragments facilitates formation of the eutectic between the bromate and bromide [2] with greater ease than that in the unirradiated sample, and hence decomposition in the irradiated samples is enhanced.

A comparison of the E value for the thermal decomposition of irradiated KBrO$_3$ [1] with that for the decomposition of NaBrO$_3$ reveals that the extent of lowering of E by irradiation is higher for NaBrO$_3$. This is due to the higher susceptibility of NaBrO$_3$ to radiation damage [19].

TABLE 3

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

Parameter	NaBrO$_3$	NaBrO$_3$ irradiated to			
		100 Mrad	200 Mrad	300 Mrad	400 Mrad
Slope	-40.8795	-37.6612	-33.2697	-28.7278	-26.9955
Intercept	56.9061	53.4876	47.2199	40.6733	38.3138
r	0.9969	0.9832	0.9923	0.9965	0.9936
E (kJ mol^{-1})	351.1	324.2	287.6	249.7	235.2
Z (s^{-1})	5.2×10^{24}	1.7×10^{23}	3.2×10^{20}	4.6×10^{17}	4.4×10^{16}

Mechanism of reaction from non-isothermal TG traces

The mechanism of the thermal decomposition reaction of NaBrO$_3$ was established by following the non-isothermal method discussed by Sestak and Berggren [7] and Satava [8]. The details regarding the computational approach for obtaining the correct mechanism and the corresponding E and Z values have already been discussed [15]. The functional values of ln $g(\alpha)$ required for this purpose were taken from the table of Nair and James [20] and E was calculated by the method of Sestak [21] from the slope. For almost the same value of r, the operating mechanism was chosen by the non-mechanistic equation. It was found that the R$_3$ mechanism [7] gives the maximum correlation (Table 3).

It can be seen from Table 3 that the decomposition of NaBrO$_3$ (both unirradiated and irradiated) follows the Avrami equation [22], $1 - (1 - \alpha)^{1/3} = kt$, and the rate-controlling process is a phase boundary reaction assuming spherical symmetry [8]. The agreement of the values of E and Z obtained using the mechanistic equation (Table 3) with those obtained using the non-mechanistic equation (Table 2) confirms this mechanism.

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