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Note

The effect of doping on the thermal decomposition of strontium bromate

S.M.K. Nair *, T.S. Sahish

Department of Chemistry, University of Calicut, P.O. Calicut University, Kerala-673 635, India

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Abstract

The thermal decomposition of strontium bromate doped with $KBrO_3$, $Mg(BrO_3)_2$, $Al(BrO_3)_3$ and KBr (10^{-4} to 10^{-1} M), was studied by dynamic thermogravimetry and the kinetic parameters were computed using the Coats–Redfern and Horowitz–Metzger equations. Doping enhances the decomposition and decreases the energy of activation in samples doped with $Al(BrO_3)_3$ and KBr, whereas $KBrO_3$ and $Mg(BrO_3)_2$ increase the thermal stability of $Sr(BrO_3)_2$.

Keywords: Activation energy; Decomposition; Doping; DTG; Strontium bromate

1. Introduction

The effect of γ-irradiation on the thermal decomposition of alkali and alkaline earth bromates has been studied in detail and the decomposition kinetics and mechanism have been fairly well established [1–4]. Possible changes in the thermal stability of $NaBrO_3$ due to doping have also been reported from this laboratory [5]. It was of interest, therefore, to extend such studies to other bromates and the present studies were undertaken. The dynamic thermogravimetric method was used as before [1].

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* Corresponding author.

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2. Experimental

$Sr(BrO_3)_2$, $Mg(BrO_3)_2$ and $Al(BrO_3)_3$ were synthesized by the method already reported [6] and the purity estimated [7]. By repeated recrystallization, 99.5% pure samples were obtained. All other chemicals used were of AnalaR grade (BDH).

Crystals of $Sr(BrO_3)_2$ doped with $KBrO_3$, $Mg(BrO_3)_2$, $Al(BrO_3)_3$ and KBr (10^{-4}–10^{-1} M) were prepared by slow crystallization of solutions containing calculated amounts of $Sr(BrO_3)_2$ and the dopant at about 60°C in a water bath. The products were separated under suction, washed five times with small amounts of cold water and dried in vacuo over P_2O_5. The structure of the doped crystals was examined, but no changes in the position or the intensities of the lines in the X-ray powder diffraction photographs could be detected for the impurity levels used in these investigations. The samples, ground (200–240 mesh) and stored in vacuum over P_2O_5, were used for the studies.

The thermograms were recorded in air using an automatically recording thermal analyser (Perkin-Elmer TGA7). The heating rate was 5°C min^{-1}. In all experiments, 10 mg of sample was used. The recorded total mass loss in all cases was 2.79 ± 0.05 mg, confirming complete conversion of strontium bromate to the bromide. The mass of material left behind after decomposition agreed with the instrument reading.

The thermal decomposition of untreated $Sr(BrO_3)_2$ (sample 1), $Sr(BrO_3)_2$ doped with $KBrO_3$ (samples 2–5), $Sr(BrO_3)_2$ doped with $Mg(BrO_3)_2$ (samples 6–9), $Sr(BrO_3)_2$ doped with $Al(BrO_3)_3$ (samples 10–13) and $Sr(BrO_3)_2$ doped with KBr (samples 14–17) was studied.

Three non-isothermal runs were taken for each sample and the mass loss–temperature relationship was reproducible. Replacement of air by nitrogen had no effect on the decomposition.

3. Results and discussion

The recorded TG traces were redrawn as mass vs. temperature (TG) curves normalizing the initial mass of samples to 100 mg (Fig. 1).

The kinetic parameters for the decomposition of $Sr(BrO_3)_2$ and the doped samples were calculated using the Coats–Redfern equation [8] in the form applicable for a first-order process, and also by the Horowitz–Metzger method [9]. The method of calculation in each case has already been reported [1].

The results are presented in Table 1. The values of the activation energy E obtained by using the two equations show good agreement, within 6%.

$Sr(BrO_3)_2$ decomposed according to the equation

$$Sr(BrO_3)_2 \rightarrow SrBr_2 + 3O_2 \quad (1)$$

The residue contained 100% bromide. The decomposition $Sr(BrO_3)_2$ in the present studies begins at 265°C which is 8°C higher than that reported by Bancroft and Gesser [6]. Doping raises the temperature at which the decomposition begins T_i by

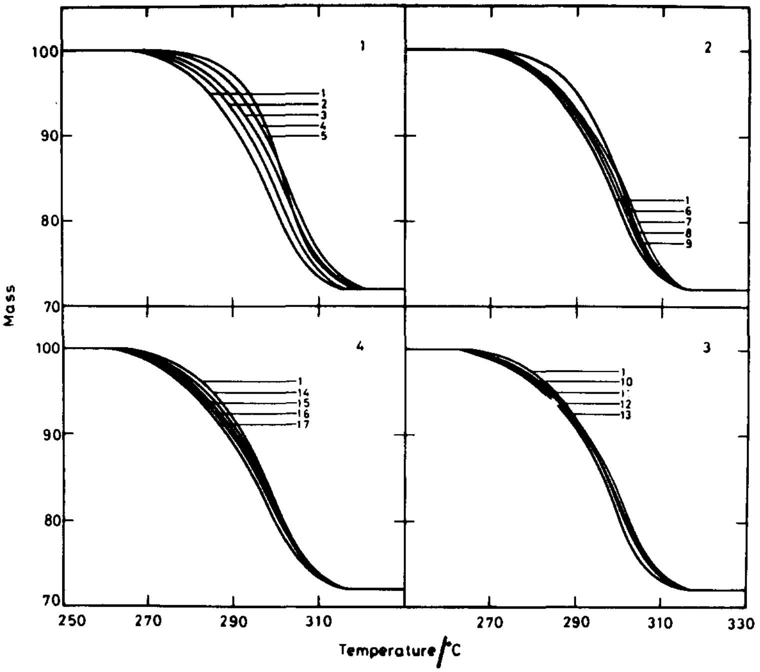

Fig. 1. TG curves of untreated and doped samples of strontium bromate: 1, untreated strontium bromate; 2, 10^{-4} M; 3, 10^{-3} M; 4, 10^{-2} M; 5, 10^{-1} M potassium bromate; 6, 10^{-4} M; 7, 10^{-3} M; 8, 10^{-2} M; 9, 10^{-1} M magnesium bromate; 10, 10^{-4} M; 11, 10^{-3} M; 12, 10^{-2} M; 13, 10^{-1} M aluminium bromate; 14, 10^{-4} M; 15, 10^{-3} M; 16, 10^{-2} M; 17, 10^{-1} M potassium bromide.

5°C in samples doped with $KBrO_3$ (samples 3–5) and $Mg(BrO_3)_2$ (samples 6–9). However, in the case of samples doped with $Al(BrO_3)_3$ and KBr, T_i is lowered by 5°C (Table 1). The temperature of completion of decomposition T_f is raised only in the case of samples doped with $KBrO_3$. For all the remaining samples, T_f and the peak temperature T_s remains unchanged (Table 1).

It can be seen from Table 1 that E increases with increase in concentration of the dopant (samples 2–5 and 6–9) and that the effect is more pronounced in the case of $Sr(BrO_3)_2$ doped with $KBrO_3$. E is increased by $\approx 34\%$ in $Sr(BrO_3)_2$ doped with $KBrO_3$ at a concentration of 10^{-1} M, whereas it is increased by $\approx 16\%$ only in the case of $Sr(BrO_3)_2$ doped with $Mg(BrO_3)_2$ at the same concentration. However, in the case of samples doped with $Al(BrO_3)_3$ and KBr (samples 10–13 and 14–17), the activation energy decreases with increase in concentration of the dopant as seen in the case of $NaBrO_3$ [5]. The decrease in E is greater in samples doped with KBr than that in samples doped with $Al(BrO_3)_3$.

Thus, it can be seen that the thermal stability of $Sr(BrO_3)_2$ is improved on doping the salt with $KBrO_3$ and $Mg(BrO_3)_2$, whereas the thermal stability is decreased on doping with $Al(BrO_3)_3$ and KBr.

Incorporation of a cationic impurity having a charge different from that of the corresponding ion in the host lattice generates defects in the host lattice [10]. It has

Table 1

Thermal decomposition data and kinetic parameters calculated using the Coats–Redfern (C–R) and Horowitz–Metzger (H–M) methods

	Sample: $Sr(BrO_3)_2$		T_i/ °C	T_f/ °C	T_s/ °C	Kinetic parameters							
						C–R				H–M method			
						E/ (kJ mol^{-1})	Z/ min^{-1}	ΔS/ (J K^{-1} mol^{-1})	Correlation coefficient r	E/ (kJ mol^{-1})	Z/ min^{-1}	ΔS/ (J K^{-1} mol^{-1})	Correlation coefficient r
1	Untreated		265	315	305	295	1.7×10^{26}	252	0.9968	298	5.0×10^{26}	261	0.9996
2	Doped K^+	10^{-4} M	265	315	305	296	2.0×10^{26}	253	0.9972	310	6.2×10^{27}	282	0.9975
3		10^{-3} M	270	320	305	301	4.8×10^{26}	260	0.9988	319	3.8×10^{28}	297	0.9985
4		10^{-2} M	270	320	305	356	4.2×10^{31}	355	0.9927	355	8.3×10^{31}	361	0.9968
5		10^{-1} M	270	320	305	395	1.5×10^{35}	423	0.9953	402	4.7×10^{37}	452	0.9917
6	Doped Mg^{2+}	10^{-4} M	270	315	305	305	1.9×10^{26}	253	0.9979	300	7.8×10^{26}	264	0.9994
7		10^{-3} M	270	315	305	301	5.3×10^{26}	261	0.9950	299	5.9×10^{26}	262	0.9991
8		10^{-2} M	270	315	305	313	8.8×10^{27}	285	0.9983	317	2.8×10^{28}	294	0.9985
9		10^{-1} M	270	315	305	343	4.0×10^{30}	335	0.9993	362	3.2×10^{32}	372	0.9991
10	Doped Al^{3+}	10^{-4} M	260	315	305	293	1.5×10^{26}	251	0.9950	298	4.6×10^{26}	260	0.9985
11		10^{-3} M	260	315	305	271	1.7×10^{24}	213	0.9938	279	8.0×10^{24}	226	0.9968
12		10^{-2} M	260	315	305	263	2.3×10^{23}	197	0.9957	267	5.9×10^{23}	205	0.9993
13		10^{-1} M	260	315	305	251	1.7×10^{22}	175	0.9938	259	1.1×10^{23}	191	0.9945
14	Doped KBr	10^{-4} M	260	315	305	279	7.0×10^{24}	225	0.9959	283	1.8×10^{25}	233	0.9988
15		10^{-3} M	260	315	305	268	8.0×10^{23}	207	0.9980	283	4.4×10^{24}	221	0.9996
16		10^{-2} M	260	315	305	252	2.3×10^{22}	178	0.9955	256	6.2×10^{22}	186	0.9993
17		10^{-1} M	260	315	305	230	1.8×10^{20}	138	0.9947	229	3.4×10^{20}	143	0.9968

also been found that homovalent impurities can produce vacancies [11] or act as electron traps [12], and these affect the sensitivity to thermal decomposition [6]. The defects introduced by doping generate free space and local strain, and the strain distorts the structure of the crystal and alters the frequency of the photon vibration in the lattice [13]. The relaxation time also changes in the region of the lattice surrounding the defect and a decrease in the symmetry of the host ion occurs. These factors substantially weaken the chemical bonds in the vicinity of the defect, thereby increasing the reactivity of the solid decomposition.

Cationic impurities with surface charge densities [14] ($\sigma = Ze/4\pi r^2$, where σ is the surface charge density, Ze is the charge of the dopant cation and r is its radius) that are greater or smaller than that of the host ion, were used in the present studies. The surface charge densities of K^+, Mg^{2+} and Al^{3+} are 0.0450, 0.3769 and 0.9554 respectively. It is seen that the thermal stability of the doped samples decreases with increase in surface charge density of the impurity ion.

The higher susceptibility to thermal decomposition observed in the case of $Sr(BrO_3)_2$ doped with KBr arises due to the presence of Br^- which facilitates the formation of the eutectic between the bromate and the bromide [15], compared with the untreated sample.

The mechanism of the thermal decomposition reaction of the untreated and doped samples of $Sr(BrO_3)_2$ was established by following the non-isothermal method discussed by Sestak and Berggren [16] and Satave [17]. The details

Table 2

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

	Sample $Sr(BrO_3)_2$		Parameter				
			Slope	Intercept	Correlation coefficient r	$E/(\mathrm{kJ\ mol^{-1}})$	Z/min^{-1}
1	Untreated		−34.1486	58.3877	0.9932	294.6	2.3×10^{25}
2	Doped K^+	10^{-4} M	−34.2496	58.3661	0.9967	295.4	2.2×10^{25}
3		10^{-3} M	−34.3824	58.3982	0.9978	296.5	2.3×10^{25}
4		10^{-2} M	−42.6227	72.5481	0.9898	365.5	3.2×10^{31}
5		10^{-1} M	−48.1462	81.9805	0.9911	411.7	4.0×10^{35}
6	Doped Mg^{2+}	10^{-4} M	−34.0366	58.0565	0.9961	293.6	1.6×10^{25}
7		10^{-3} M	−34.7923	59.2323	0.9898	299.9	5.3×10^{25}
8		10^{-2} M	−35.7818	61.2239	0.9958	308.2	3.9×10^{26}
9		10^{-1} M	−39.2110	66.9523	0.9983	336.9	1.3×10^{29}
10	Doped Al^{3+}	10^{-4} M	−32.9127	56.2614	0.9912	284.2	2.7×10^{24}
11		10^{-3} M	−32.2596	55.1722	0.9947	278.7	9.1×10^{23}
12		10^{-2} M	−28.6086	48.6571	0.9993	248.2	1.3×10^{21}
13		10^{-1} M	−28.1039	47.7178	0.9940	243.9	5.3×10^{20}
14	Doped KBr	10^{-4} M	−31.9866	54.6324	0.9918	276.4	5.3×10^{23}
15		10^{-3} M	−30.3094	51.7454	0.9942	262.4	3.0×10^{22}
16		10^{-2} M	−28.8358	49.1475	0.9899	250.1	2.2×10^{21}
17		10^{-1} M	−26.7419	45.5057	0.9897	232.5	5.8×10^{19}

regarding the computational approach for obtaining the correct mechanism and the corresponding *E* and *Z* values have already been discussed [1]. The functional values of $\ln g(\alpha)$ required for this purpose were taken from the table of Nair and James [18] and *E* was calculated by the method of Sestak [19]. For almost the same value of correlation coefficient *r*, the operating mechanism was chosen by a non-mechanistic equation. It was found that the maximum correlation was obtained for the R_3 mechanism.

It can be seen from Table 2 that the decomposition of $Sr(BrO_3)_2$ (both untreated and doped samples) follows the Avrami equation [20], $1-(1-\alpha)^{1/3}=kt$, and that the rate-controlling process is a phase-boundary reaction assuming spherical symmetry [14].

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