

INFLUENCE OF SO_4^{2-} DOPING AND γ -IRRADIATION ON THE THERMAL DECOMPOSITION OF BARIUM BROMATE

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The effects of SO_4^{2-} doping and γ -irradiation on the isothermal (563 K) decomposition of barium bromate have been investigated gasometrically with a vacuum apparatus. Plots of the fraction decomposed α vs. time t for pure, doped and irradiated crystals exhibited characteristic stages: initial gas evolution (initial puff), an induction period, linear reaction, an acceleratory period and decay. The data are considered in the light of various kinetic models, e.g. linear rate equation, Prout-Tompkins and Avrami-Erofeev. The plausible mechanism of the reaction and the effects on this of anion vacancies and γ -irradiation are discussed briefly.

The thermal decomposition of solids is an important field of solid-state chemistry, with vast technical applications [1, 2]. The understanding and control of the chemical reactivity of solids are the main objects in decomposition studies [3]. As ammonium perchlorate (AP) is extensively used as a solid propellant and more generally in pyrotechnic systems [4], a detailed study is needed on the decomposition of inorganic oxyanions such as chlorates, bromates and perchlorates, and on how this is influenced by vacancies (cation and anion) and irradiation. Barium bromate, which decomposes entirely in the solid phase, was chosen for the present study. Although the effects of cation vacancies and γ -irradiation on the decomposition of its crystals have been well studied [5–8], the available data on the effects of anion vacancies are inadequate. The present investigation relates to the effects of SO_4^{2-} doping and γ -irradiation on the isothermal decomposition of barium bromate.

Experimental

Barium bromate was prepared from AR grade chemicals and was purified by repeated recrystallization. Doped (SO_4^{2-} , 1.0 mol%) crystals of barium bromate

were prepared by coprecipitation from a solution of the corresponding salts in the required proportions and was characterized by X-ray diffraction analysis. Pure crystals were sealed in *vacuo* in pyrex glass ampoules and were irradiated with 1.0 MGy of ^{60}Co γ -rays at a dose rate of 0.1×10^{-2} MGy h^{-1} . Gasometric study of the decomposition was carried out at 563 K by adopting the procedure described earlier [9]. About 2.0×10^{-1} g of the salt was decomposed and course of the reaction was followed by oxygen pressure measurements. The fraction decomposed, $\alpha(p/p_f)$, was calculated from the pressure p at any time t , and the pressure p_f on complete decomposition.

Results and discussion

The α -vs- t plots (Fig. 1) for pure, doped and irradiated barium bromate exhibit characteristic stages: initial gas evolution or initial puff, a short induction period, a slow linear reaction followed by an acceleratory stage and decay. The α value for the initial burst of gas ($\alpha \sim 0.04$) remains unaffected by doping, but is enhanced ($\alpha \sim 0.06$) upon irradiation. The initial pressure rise in the vacuum system, which is possibly due to the release of occluded air, is far too rapid to allow determination of its kinetics.

The induction period I is shortened both by SO_4^{2-} doping and by γ -irradiation. The values for pure, doped and irradiated crystals are 22.0, 12.0 and 8.0 min, respectively. During this stage, the reaction proceeds very slowly [10, 11], as a result of which the product gas pressure remains virtually constant over a considerable range, the duration of the induction period being a function of the experimental

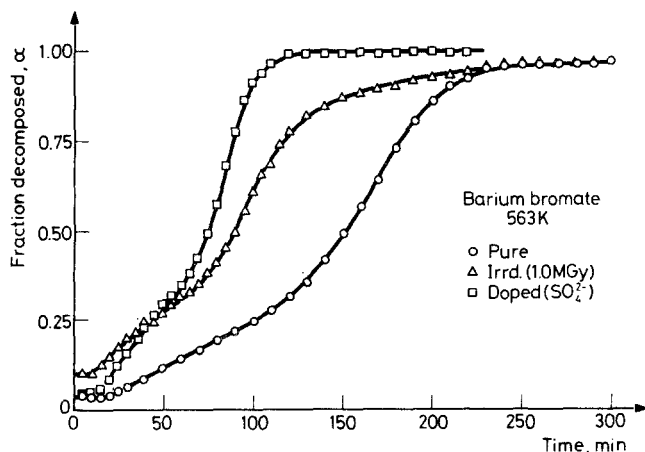


Fig. 1 Influence of SO_4^{2-} doping and γ -irradiation on the decomposition of barium bromate at 563 K

temperature and the irradiation dose applied. The reaction nucleates [12] at energetically favourable sites in this period. The data indicate that the effect of irradiation is more prominent than that of anion vacancies, which may be due to an increase in the density of nucleation centres within the crystal lattice. The rate constant for this stage is determined from

$$1/t = k_1 \quad (1)$$

where t is the time at which the induction period diverges from linearity [12]. In the present case, it is not possible to determine the kinetics for this period, as it is very small.

The induction period is followed by the linear stage, represented as

$$\alpha = k_2 t + C_2 \quad (2)$$

where k_2 is the rate constant and C_2 is another constant; the former increases with increase of temperature. Both SO_4^{2-} doping and γ -irradiation (Table 1) enhance the rate in the linear stage (Fig. 2), the former being more effective than the latter,

Table 1 Influence of SO_4^{2-} doping and γ -irradiation on the thermal decomposition of barium bromate at 563 K

State of $\text{Ba}(\text{BrO}_3)_2$	Linear rate constant $k_2 \times 10^2 \text{ min}^{-1}$	Acceleratory rate constant, $k_{3,5} \times 10^2 \text{ min}^{-1}$		Decay rate constant, $k_{4,6} \times 10^2 \text{ min}^{-1}$	
Pure	0.25	0.80	(P-T)	1.62	(P-T)
		0.33	(A-E)	0.73	(A-E)
SO_4^{2-} doped	0.69	1.62	(P-T)	7.70	(P-T)
		0.78	(A-E)	3.13	(A-E)
Irrad. 1.0 MGy	0.49	1.56	(P-T)	0.72	(P-T)
		0.8 ^a	(A-E)	0.35	(A-E)

P-T: Prout-Tompkins relationship

A-E: Avrami-Erofeev relationship

which may be due to the presence [13] of a higher number of reactive nucleation centres in the crystal lattice. The reaction taking place in this stage is well explained [14] by the penetration of nuclei of approximately constant area into the bulk from the surface, the surface nucleation being instantaneous or at least very rapid.

The linear stage is succeeded by a sigmoidal regime consisting of acceleration and decay, analysed according to various kinetic equations: the Prout-Tompkins [15] relationship (Fig. 2):

$$\log(\alpha/1-\alpha) = k_{3,4} t + C_{3,4} \quad (3)$$

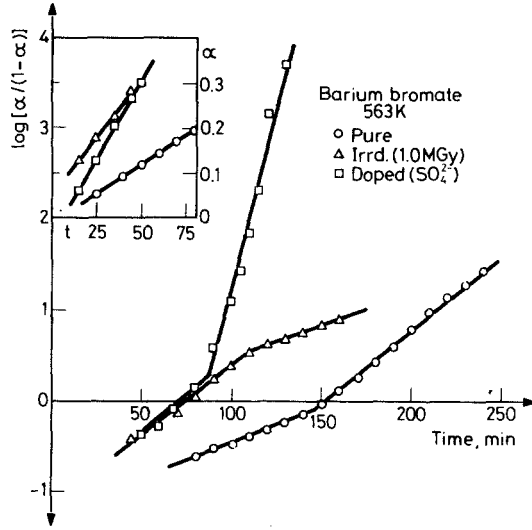


Fig. 2 Influence of SO_4^{2-} doping and γ -irradiation on the linear, acceleratory and decay stages of decomposition of barium bromate at 563 K

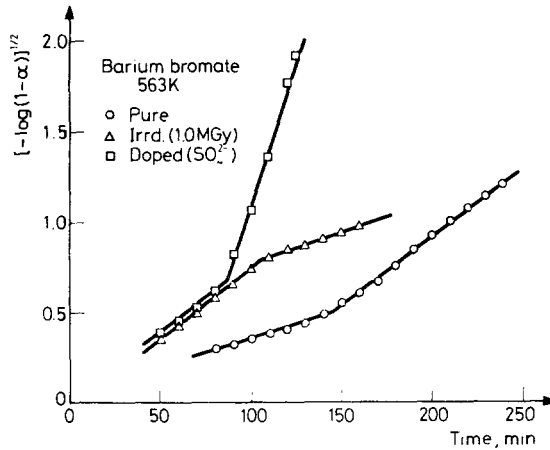


Fig. 3 Influence of SO_4^{2-} doping and γ -irradiation on the acceleratory and decay stages of decomposition of barium bromate at 563 K

and the Avrami–Erofeev [16] formula with $n=2$ (Fig. 3):

$$[-\log(1-\alpha)]^{1/2} = k_{5,6}t + C_{5,6} \tag{4}$$

where k_3 and k_5 are the rate constants for the acceleratory stage, and k_4 and k_6 are those for the decay stage. The ranges of applicability of Eqs (3) and (4)

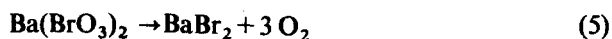
are $0.20 < \alpha < 0.97$ and $0.20 < \alpha < 0.97$ (pure); $0.28 < \alpha < 0.89$ and $0.30 < \alpha < 0.89$ (irrad.); $0.30 < \alpha < 0.99$ and $0.30 < \alpha < 0.99$ (doped), respectively. It is evident from the data (Table 1) that both treatments enhance the rate of the acceleratory stage to the same extent when analysed via Eqs (3) and (4), but the decay stage is accelerated by SO_4^{2-} doping and is retarded by irradiation.

In the sigmoidal decomposition region, the rate of the reaction initially increases (acceleratory stage) with time until a maximum is attained, which is ascribed to the formation of additional nuclei due to the strain exerted [17] by the growing nuclei and the autocatalytic effect [18, 19] of the solid product phase. The product layer generated during the initial slow reaction increases in thickness on the crystal faces until sufficient strain is produced to initiate cracks. In the present study, this point is reached at a critical thickness of the product material corresponding to $\alpha \sim 0.22$. The reaction thereafter proceeds down these cracks in a branching manner, as postulated in the Prout–Tompkins [15] relationship for solid-state decomposition. As regards the autocatalytic effect of the solid product phase, the bromide ions generated by decomposition have a certain mobility and appear to catalyse [9] the decomposition of bromate ions. The decay stage of the sigmoidal regime is attributed to the fact that the nuclei formed in the crystal lattice overlap [20, 21], as a result of which the whole surface undergoes decomposition and further nucleation does not occur. However, the central regions of the crystal still contain some undecomposed material, which is responsible for further reaction [20, 21], causing a progressive decrease in the area of the reactant product interface, resulting [23] in retardation of the reaction.

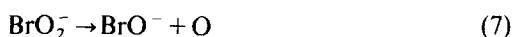
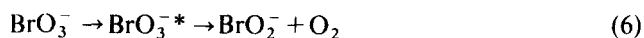
As the sigmoidal regime of the decomposition satisfactorily fits the Avrami–Erofeev [16] equation with $n=2$, it is implied that the crystals undergo decomposition by random nucleation followed by two-dimensional growth of the nuclei.

Chemistry of thermal decomposition

Bircumshaw and Newman [24] suggested three mechanisms for the decomposition of solids: (i) electron transfer, (ii) proton transfer, (iii) breakdown of the anion or rupture of a bond; they assigned the low-temperature decomposition to (i) and the high-temperature one to (ii) and (iii). According to Pauling [25], the energy of the “Br–O” bond is of the order of $229.0 \text{ kJ mol}^{-1}$, which is also found [5–8] for the decomposition of barium bromate. Many workers have postulated that the primary step in the decomposition is rupture of the bromine-oxygen bond, which takes place as [26]



The unstable intermediates generated during the process are



The formation of micromolecular amount of bromide in the reaction matrix of bromate may also influence the rate of the reaction by involving electron transfer [7] as a catalytic effect during the heating process.

Role of SO_4^{2-} doping

In the temperature range studied in the present case, the decomposition of barium bromate is most plausibly dominated [27, 28] by the Schottky disorder, where the relation between the vacancy concentrations is:

$$[+][-] = \text{constant at constant temperature}$$

The incorporation of SO_4^{2-} ion into the barium bromate lattice increases the anion vacancy concentration and enhances the rate of decomposition, probably because of the development of an excess of electron traps. Other contributing factors [6, 29] for an acceleration of the rate are the free space and local strain generated by doping (anion). The strain distorts the structure of the crystal and alters the frequency of the phonon vibration in the lattice. There is also change in the lattice surrounding the defect, and a decrease in the symmetry of the bromate ion occurs. These factors substantially weaken the "Br-O" bond in the vicinity of the defect, thereby influencing the reactivity of the solid.

Role of irradiation

When barium bromate is exposed to ^{60}Co γ -rays, apart from trapped electrons and holes, there will be atoms, radicals and ions in the interstitial positions, while fragments bearing the same charge as the parent ion will be present in the lattice positions. Under the present experimental conditions, the entities [30] generated in the irradiated crystals are Br^- , BrO^- , BrO_2^- , BrO_4^- , O_3^- , O , O_2 and e_t .

The oxygen formed in this way remains trapped in the crystal and is released immediately on heating. The initial gas evolution is therefore higher for the irradiated crystals than for the pure and doped substances. The radiolytic fragments constitute decomposition nuclei themselves and may be termed irradiation nuclei. Upon subsequent heating, they grow in size or in number and

the induction period continues until a critical number of nuclei n_c is attained [10, 11]. Thus, the density of nucleation centres within the crystal lattice increases, resulting in a reduction in the time required to attain n_c , thereby shortening the induction period I. As the rate of the linear stage reaction is a function of the concentration of potential nucleus-forming sites present on the surface of the lattice, the presence of a larger number of such nuclei in the irradiated crystals enhances the rate effectively.

The significant increases in the rate constants k_3 (P-T) and k_5 (A-E) (Table 1) for the acceleratory stage of the irradiated salt may be attributed to the increase in the density of potential nucleation centres [31] and the catalytic effect of bromide generated by irradiation; the concentration of this ion in the decomposing irradiated solid at the end of the acceleratory period is higher than that in the pure or the doped substance. When the decomposition passes over to the deceleratory stage, the rate of the reaction depends upon the amount of bromate left undecomposed at a given time. The observed retardation, reflected in the rate constants (k_4 and k_6) (Table 1) may arise from the fact that irradiation enhances the decomposition in the acceleratory stage, and consequently reduces the concentration of undecomposed molecules. As a result of this, the reactant-product interface contains a smaller number of reactive molecules [32] (barium bromate) at the commencement of the decay period causing deceleration.

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Zusammenfassung — Die Wirkung von Versetzen mit SO_4^{2-} und γ -Bestrahlung auf die isotherme (563 K) Zersetzung von Bariumbromat wurde gasometrisch untersucht. Es zeigte sich, daß die Zeitcharakteristiken für die reinen, die versetzten und bestrahlten Kristalle verschiedene Stufen durchlaufen, nämlich anfängliche Gasentwicklung (Aufblähen), Induktionsperiode, lineare Reaktion, Beschleunigung und Abklingen. Die Daten wurden unter dem Gesichtspunkt verschiedener kinetischer Modelle betrachtet, z. B. lineare Geschwindigkeitsgleichung, das Modell von Prout-Tompkins und Avrami-Erofeev. Es werden kurz ein einleuchtender Reaktionsmechanismus und der Einfluß von Anionengitterlücken und γ -Bestrahlung darauf diskutiert.

Резюме — Методом газометрии изучено влияние легирующей добавки сульфат-иона и γ -облучения на изотермическое разложение (563 К) бромата бария. Наблюдалось, что фракция разложения, α -время, « t » характеристики для чистых, легированных и облученных кристаллов показывают такие стадии, как начальное выделение газа, индукционное время, линейную реакцию, ускорение и распад. Полученные данные рассматривались в свете различных кинетических моделей подобно уравнению линейной скорости, уравнениям Прот-Томпкинса и Авраами-Ерофеева. Кратко обсужден приемлемый механизм реакции и влияние на него анионных вакансий и облучения.