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INFLUENCE OF ADDITIVES ON THE SOLID PHASE THERMAL DECOMPOSITION OF BARIUM BROMATE

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ABSTRACT

The influence of a number of additives (CuO, Cr_2O_3, TiO_2 and Al_2O_3) on the solid phase thermal decomposition of barium bromate has been investigated at 563 K. It is seen that the fraction decomposed versus time ($\alpha - t$) characteristics for pure crystals and for mixtures exhibit stages: (i) initial rapid gas evolution, (ii) short induction period, (iii) slow linear reaction, followed by (iv) acceleratory stage and decay. The data are analysed according to Prout–Tompkins kinetics. It is seen that irrespective of the semiconductive properties of the oxides, the initial gas evolution is the same ($\alpha \sim 0.04$) in all cases, and that the additives shorten the duration of the induction period. The oxides, CuO and TiO_2 being p- and n-type semiconductors, respectively, enhance the rate constants of the linear and acceleratory stages. However, CuO retards the rate of the decay period, whereas TiO_2 does not affect it. The p-semiconductive oxide, Cr_2O_3, decelerates the rate of all the stages. Al_2O_3 (an insulator) has a marginal effect on the reaction rates.

INTRODUCTION

Many workers [1–5] have studied the solid phase thermal decomposition of various oxysalts of halogens (i.e. chlorates, bromates and perchlorates of alkali and alkaline earth metals) and the role of doping and irradiation thereon using TGA, DTA, DSC and gas pressure measurements. It has been reported that both doping and irradiation shorten the induction period and enhance the rate of decomposition. Data on the influence of additives on the thermal decomposition of inorganic molecular ions [6–8] show that the most active metal oxides are those of transition metals. The defect nature of the oxide plays an important role in the catalytic efficiency with respect to the thermal decomposition of solids. Boldyreva and Mozzhova [9] have studied the role of additives (CdO, ZnO and PbO) on the thermal decomposition of ammonium perchlorate and suggested that there is a chemical reaction

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between the components of the mixtures investigated. It is of interest to study the role of additives (metal oxides with different semiconductive properties) on the thermal decomposition of barium bromate, on which the influence of doping and irradiation has been extensively studied [5,10].

EXPERIMENTAL

AR grade barium bromate, monohydrate was dehydrated to constant weight at 170 °C in a thermostatted electric hot air oven and the anhydrous material was stored over phosphorus pentoxide. The additives CuO, Cr_2O_3, TiO_2 and Al_2O_3 were of BDH laboratory reagent grade. All bromate–catalyst mixtures (10% w/w) were weighed in the proper ratios. They were then thoroughly mixed using an agate mortar and pestle, dried and stored in a desiccator. The isothermal decomposition study was carried out at 568 K by gas pressure measurement using a vacuum apparatus following the procedure described earlier [1]. The fraction decomposed ($\alpha = p/p_f$) was calculated from the pressure value p at any time t, and p_f the final pressure on complete decomposition.

RESULTS AND DISCUSSION

The fractional decomposition α versus time plots for the isothermal decomposition of pure salt and of mixtures are presented in Fig. 1. It is seen that the decomposition proceeds through various stages: (i) initial gas evolution, (ii) short induction period, (iii) a slow linear reaction, followed by (iv) a sigmoidal zone consisting of an acceleratory stage and decay. The initial gas evolution, $\alpha \sim 0.04$, is the same in all cases and is possibly due to the release of occluded air. It is far too rapid for the kinetics to be determined.

As in the examples of irradiation and doping reported in refs 1, 2, 5 and 10 the additives in this study also shorten the induction period (Table 1). The lengths of the induction periods follow the order

$$TiO_2 < CuO < Cr_2O_3 \sim Al_2O_3 < \text{pure salt}$$

During the induction period, the reaction nucleates at energetically favourable sites; the nuclei are relatively small initially and grow to a larger size during the acceleratory stage [1–3]. The reaction proceeds extremely slowly in this period and the pressure of the product gas remains virtually constant over a considerable range, i.e. during the duration of the induction period. The shortening of this period indicates that nucleation of the decomposition process is rapid in the presence of additives.

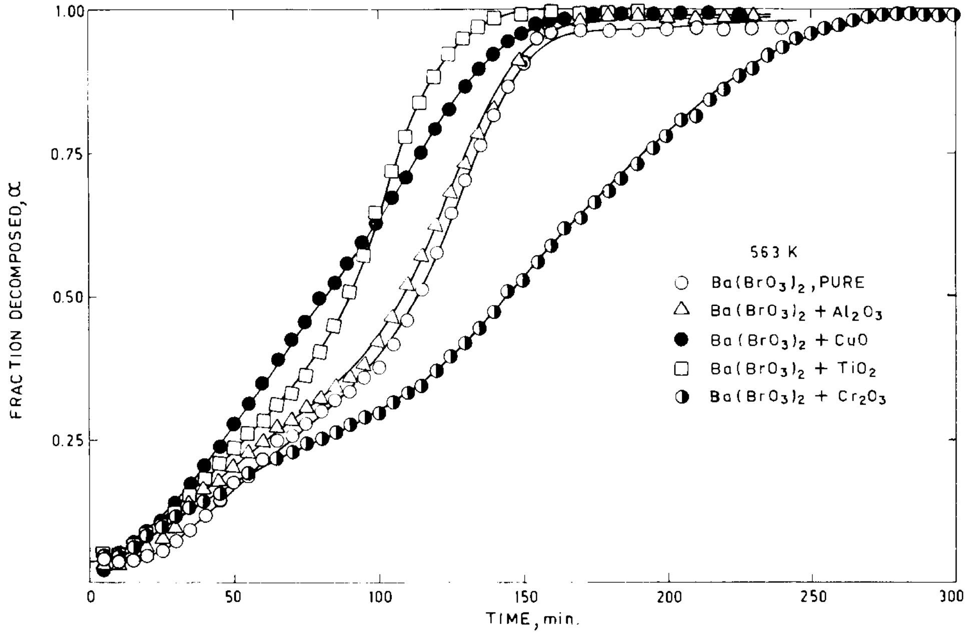

Fig. 1. Role of additives on the isothermal decomposition of barium bromate at 563 K.

The slow reaction following induction is represented (Fig. 2) by the linear relationship

$$\alpha = k_1 t + C_1 \tag{1}$$

where k_1 and C_1 are constants. Both CuO and TiO_2 enhance the rate of the linear stage, the effect being more prominent in CuO. Cr_2O_3 decelerates the rate and Al_2O_3 has almost no effect on the process. The linear reaction stage following induction [1] may be attributed to surface decomposition, caused by the growth of the nuclei formed during induction. The enhancement in the rate may occur as a result of the favourable growth of nuclei.

TABLE 1

Influence of additive (Al_2O_3, CuO, Cr_2O_3 and TiO_2) on the solid phase thermal decomposition of barium bromate at 563 K

Substance	Initial gas evolution α	Induction period (min)	Linear rate constant k_1 ($\times 10^2$ min^{-1})	Acceleratory rate constant k_2 ($\times 10^2$ min^{-1})	Decay rate constant k_3 ($\times 10^2$ min^{-1})
Pure $Ba(BrO_3)_2$	0.040	22	0.46	0.80	3.36
$Ba(BrO_3)_2 + Al_2O_3$	0.035	12	0.48	0.87	2.94
$Ba(BrO_3)_2 + CuO$	0.035	10	0.63	1.23	2.66
$Ba(BrO_3)_2 + Cr_2O_3$	0.040	12	0.37	0.71	1.07
$Ba(BrO_3)_2 + TiO_2$	0.040	6	0.57	1.53	3.36

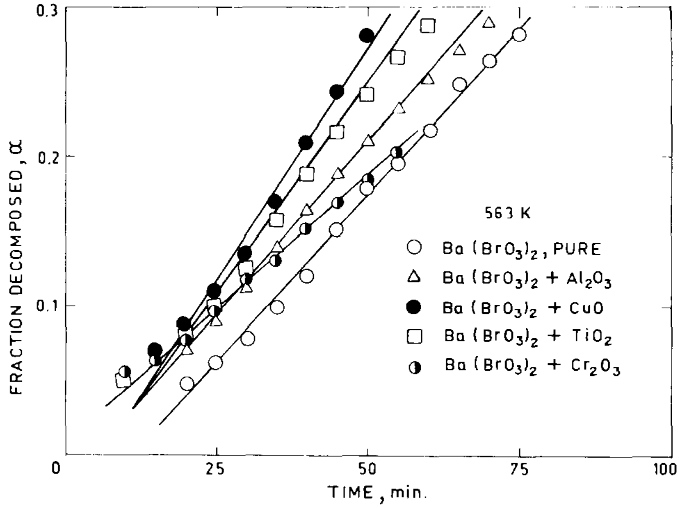

Fig. 2. The linear stage reaction of pure and catalyst mixtures of barium bromate at 563 K.

Data for the sigmoidal zone are analysed according to the Prout–Tompkins [11] relationship (Fig. 3)

$$\log[\alpha/(1-\alpha)] = k_{2,3} + C_{2,3} \quad (2)$$

where k_2 and k_3 are rate constants for the acceleratory and the decay

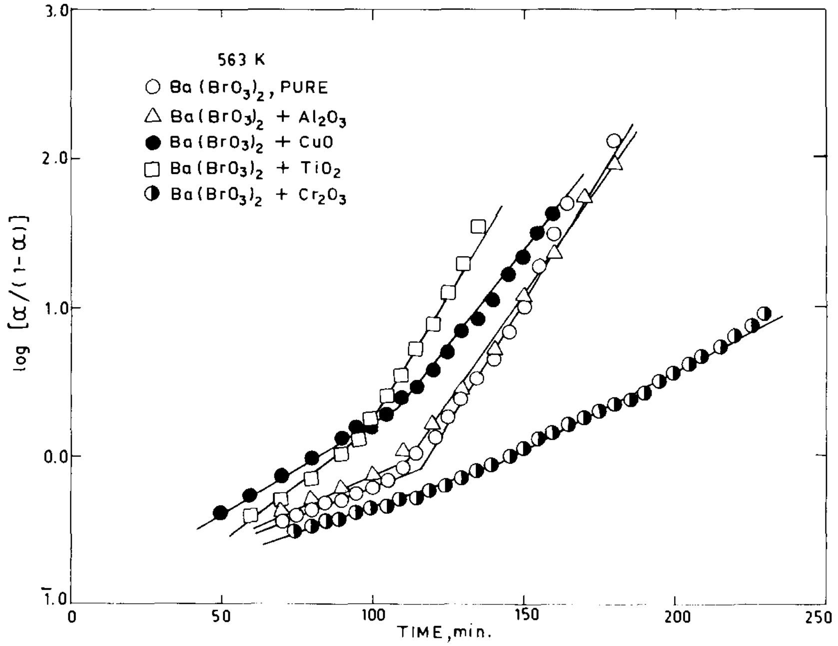

Fig. 3. The Prout–Tompkins Relationship in pure and catalyst mixtures of barium bromate at 563 K.

stages, respectively. The data show that both CuO and TiO_2 enhance the rate constant of the acceleratory period. However CuO retards the rate of the decay stage, whereas TiO_2 does not affect it. Cr_2O_3 reduces the rate of the acceleratory and decay stages. Al_2O_3 has little influence on the reaction rates. In the sigmoidal decomposition region, the rate initially increases with time until a maximum is attained. The observed increase in the rate of decomposition for the acceleratory stage may be attributed to two factors: the strain exerted by the growing nuclei and the autocatalytic effect of the solid product phase (bromide ion formed during decomposition) [1,2,5,10]. Deceleration in the decomposition rate probably occurs as a result of the following factors [7]: (a) a decrease in the catalytic activity as decomposition progresses; (b) a decrease in the flux of bromate ions adsorbed on the catalyst surface.

ROLE OF CATALYST ON DECOMPOSITION PROCESS

Barium bromate begins to decompose at 553 K, the decomposition occurring entirely in the solid phase [12] following the equation

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

The thermal decomposition behaviour of this substance under the condition of a progressive rise in temperature was studied by Hackspill and Winterer [13]. They suggested the possibility of the formation of perbromate during the decomposition. However, the subsequent work of Bancroft and Gesser [12] ruled out this idea. Various unstable intermediates generated during the decomposition are represented as

$$BrO_3^- \rightarrow BrO_2^- + O$$

$$BrO_2^- \rightarrow BrO^- + O$$

$$BrO^- \rightarrow Br^- + O$$

$$O + O + Br^- \rightarrow O_2 + Br^-$$

The influence of additives (metal oxides) on the thermal decomposition of barium bromate may be explained [14] on the basis of an electron transfer mechanism

$$BrO_3^- + e(\text{solid additive}) \rightarrow BrO_2^- + O^-_{(ads)} \qquad (i)$$

$$O^-_{(ads)} \rightarrow O_{(ads)} + e(\text{solid additive}) \qquad (ii)$$

$$O_{(ads)} + O_{(ads)} \rightarrow O_2(g) \qquad (iii)$$

$$O_{(ads)} + O^-_{(ads)} \rightarrow O_2(g) + e(\text{solid additive}) \qquad (iv)$$

where step (ii) may be rate limiting. The bromate formed in step (i) may undergo decomposition as mentioned earlier. Step (ii) is expected to be the rate-determining step because it has been reported by many workers [7] that the catalytic activity of metal oxides increases in the same order as the ability of the high valent catalyst cations to accept electrons and thus to be reduced to a lower state, e.g. $Mn^{4+} + 2e \rightarrow Mn^{2+}$. Thus for the reaction in step (i) electrons are required and the subsequent reactions, collectively known [15] as the desorption reaction, furnish electrons.

On the assumption [15] that adsorbed oxygen withdraws electrons from the catalyst, thus increasing the number of positive holes, it is expected that a p-type semiconductor would be more conductive in an oxygen atmosphere as observed in the present case. A p-type semiconductor would favour step (ii) because of the presence of positive holes in the *d*-orbitals which would be available to accept electrons from an adsorbed oxide ion. Dowden [16] reported that for oxygen reactions the p_d-type oxides are more active. In n-type semiconductive oxides, the delocalized electrons in the conduction band contribute to their electrical conductivity. On heating these oxides at high temperature in an oxygen atmosphere, the number of electrons in the conduction band decreases, leading to lower electrical conductance of the oxide [6]. Under similar conditions, an n-type oxide takes up very little oxygen as $O^-_{(ads)}$ compared with a p-type oxide and hence is a poor catalyst [15].

Although Cr_2O_3 (p-semiconductor) shows high electrical conductivity (corresponding to its high catalytic activity), a partial or complete electron transfer results in an apparently irreversible change in the oxidation state of the metal ion, which may be oxidised by bromate to chromate possibly as a result of a redox reaction $Cr_2O_3 \rightarrow CrO_4^{2-}$.

Although many workers [4,7,15–17] have agreed to the conclusion that p-type semiconductors are good catalysts and n-type are poor catalysts, the present data are not in agreement with their views. This leads to the conclusion that the behaviour of metal oxide catalysts on thermal decomposition reactions may not solely be based on the semiconductive properties of the oxides. This may be a result of the specificity of catalysts for each reaction.

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