EFFECT OF ANION DOPING ON THE THERMAL DECOMPOSITION OF POTASSIUM BROMATE

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Abstract

Structural defects were introduced into the potassium bromate (PB) lattice in the form of SO_4^{2-} and Cl^- ions in the process of crystal growth. It was assumed that these doped crystals $PB(Cl^-)$ and $PB(SO_4^{2-})$ are composed of a two phase system, one being the perfect PB lattice and the other distorted regions due to induced defects. Isothermal decomposition of doped and normal PB samples was carried out gasometrically between the temperature range 653–663 K. The α-t plots reveal that the process occurs through initial gas evolution, acceleratory and decay stages. It also confirmed that doping enhances the rate of the reaction, the effect being more pronounced in the case of $PB(SO_4^{2-})$. The data are found to be well fitted to the Prout-Tompkins and Avrami-Erofe'ev mechanisms.

Keywords: anion doping, defects, isothermal decomposition

Introduction

Extensive work has been done on the thermal behaviour of alkali metal halates [1–9] which are characterised by their oxygen generating capacity on decomposition. This is of importance as chemical transformation of solids play a significant role in modern technology [9]. Several investigations have been carried out on the effect of additives [1, 5] irradiation [4, 6, 7] and dopants [2–4, 7, 8] on the thermal decomposition of halogen oxosalts. It has been reported that irradiation increases the rate of decomposition by lowering the energy of activation [2] which may be attributed to the lattice defects generated, chemical damage fragments and products of decomposition. Lattice defects introduced during crystal growth, even at low density, influences the most characteristic features of the host crystals [9]. Diffusion which depends on the presence and movement of defects, plays a vital role in solid state reactions. Observations reveal that thermal properties of doped inorganic solids change especially in the vicinity of phase transition temperature [10]. The thermal decomposition of PB is characterised by the fact that it proceeds through a molten/semi-molten state due to the formation of an eutectic below the melting point of the substance [5, 8]. It was

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therefore of interest to study the effects of the induced defects as doped anions on the thermal decomposition of PB. The present work is on the study of the comparative effect of doping by anions (Cl^- and SO_4^{2-}) having different size and valency which act as potential sites for nucleation in the solid phase and as catalysts in the molten/semi-molten phase of the decomposition as no topochemical aspects are involved at this stage [4a].

Experimental

Analar grade potassium chloride, potassium sulphate and PB were used for the preparation of samples. Crystals of potassium chloride and potassium sulphate ($5 \cdot 10^{-2}$ molar ratio) were incorporated into the lattice of PB by slow crystallisation of solutions containing calculated amount of the dopants [3, 10] and PB. The samples were dried at 430 K and were stored over P_2O_5 in desiccator. The purity and homogeneity of the samples were tested by chemical and X-ray diffraction methods. Isothermal decomposition studies of the samples were carried out (653–663 K) gasometrically in vacuum [11, 12] apparatus. The fraction decomposed $\alpha(=p_t/p_f)$ values were obtained from the pressure of the evolved oxygen at different time intervals (p_t) and at the end of decomposition (p_f) process.

Results and discussion

The isothermal decomposition of PB proceeds with evolution of oxygen according to the reaction (1) through initial gas evolution, acceleratory and decay stages.

$$KBrO_3 = KBr + 1.5O_2 \tag{1}$$

The initial gas evolution which may be due to the occluded air at the crystal surface is enhanced by increase in temperature and upon doping; the effect being more pronounced with $PB(SO_4^{2-})$ (Figs 1 and 2). α_{3min} values for PB, PB(Cl^-) and PB(SO_4^{2-}) were found to be 0.012, 0.03 and 0.06 respectively at 658 K. The absence of induction
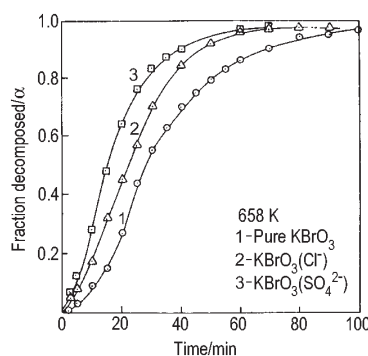

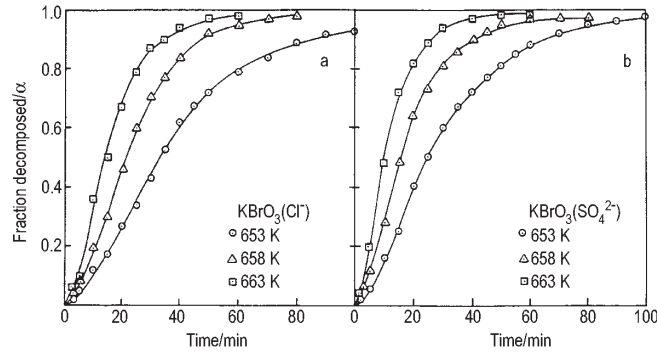**Fig. 1** Effect of doping on the isothermal decomposition of PB

Fig. 2 Effect of temperature on the isothermal decomposition of doped samples of PB

period and linear stage (Figs 1 and 2) is indicative of the fact that instantaneous nucleation takes place in the surface of normal and doped samples of PB [5, 8]. This corresponds to the applicability of kinetic models like Prout-Tompkins [13] and Avrami-Erofe'ev [14]. (Figs 3 b and a, Eqs (2) and (3) respectively.)

$$\log(\alpha/1-\alpha)=k_{A,D}+C_1 \qquad (2)$$

$$[-\log(1-\alpha)]^{1/n}=k_{A',D'}+C_2 \quad (n=2) \qquad (3)$$

$k_{A,A'}$ and $k_{D,D'}$ represent rate constants for acceleratory and decay stages respectively, C_1 and C_2 being constants. The ranges of applicability of the above equations over the sigmoidal region being $0.01<\alpha<0.86$ PB, $0.05<\alpha<0.92$ PB(Cl$^-$) and $0.05<\alpha<0.96$ PB(SO$_4^{2-}$).
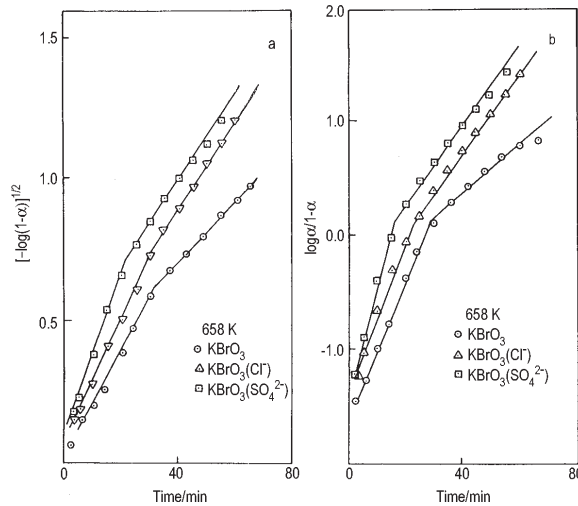

Fig. 3 Avrami-Erofe'ev (a) and Prout-Tompkins (b) analysis of data on different samples of PB

The acceleratory and decay stages are shortened upon increase of temperature and it is found that at 663 K, the reaction is almost complete after 50 min of the commencement of the decomposition for $PB(SO_4^{2-})$ whereas and same stage is reached after 70 and 80 min for $PB(Cl^-)$ and PB respectively (Figs 1 and 2). This may be attributed to the fact that the reacting mass becomes homogeneous during the acceleratory stages of the decomposition of PB due to the formation of an eutectic and DTA show that the melting point is lowered from 730 to 670 K where the onset of decomposition take place [5, 15, 16]. In this molten/semimolten stage, doping favours the decomposition to a large extent (Figs 1 and 2). This may be attributed to the catalytic activity of the product bromide ions and that of the induced defects in the crystal lattice [4a]. By displacing an ion from the regular lattice site, an induced defect introduces local strain which results in the alteration of the frequency of the phonon vibration. These changes bring about a decrease in the symmetry of the host bromate ions [17, 18] and weaken the chemical bonds in the vicinity of the doped ions leading to a marked increase in the reactivity. Table 1 indicates that the rate constants of both acceleratory and decay stages are enhanced upon doping, the effect being more in the case of $PB(SO_4^{2-})$. The applicability of Eqs (2) and (3) also points to the possibility that each product nucleus catalyzes the formation of neighbouring nuclei which is more effective in the molten state than in the solid state thus indicating that nucleation occurs in the chain branching manner and there is two dimensional growth of nuclei [7, 8].

Table 1 Effect of doping on rate constants (k_A, k_D and $k_{A'}$ and $k_{D'}$ in 10^2 min^{-1})

| Temp./ K | Prout-Tompkins | | | | | | Avrami-Erofe'ev | | | | | |
| | PB | | PB(Cl$^-$) | | PB(SO$_4^{2-}$) | | PB | | PB(Cl$^-$) | | PB(SO$_4^{2-}$) | |
	k_A	k_D	k_A	k_D	k_A	k_D	$k_{A'}$	$k_{D'}$	$k_{A'}$	$k_{D'}$	$k_{A'}$	$k_{D'}$
653	3.9	1.4	4.3	1.8	6.2	2.5	1.3	0.7	1.5	0.8	1.7	1.0
658	5.8	2.2	6.5	2.8	8.3	3.0	1.7	1.0	2.5	1.6	3.0	1.7
663	6.2	2.5	8.7	3.5	11.2	3.7	2.2	1.2	2.7	1.2	4.0	1.2

It was of interest to observe that at all temperatures (Table 1) $k_A>k_D$ and $k_{A'} >k_{D'}$ for all the samples which may be attributed to the slowing down of the decomposition process due to the presence of excess bromide ions which facilitates the resolidification of the melt and restricts the escape of oxygen [5, 8]. The enhanced rate of decomposition due to the presence of Cl^- and SO_4^{2-} can also be explained on the basis of the electron donating character of both the anions to an oxygen atom of an undecomposed bromate ion thereby promoting the splitting of the latter [15]. Depending on their valency, the incorporation of foreign ions changes the number of cation and anion vacancies and these changes induce modification in the rate of decomposition. Since anion vacancies mean a +ve charge in the crystal lattice, the higher charge on the SO_4^{2-} ion has a greater effect on the electron transfer process and hence enhanced rate of reaction results. The introduction of the bivalent ion forces two bromate ions to leave the lattice to maintain the charge neutrality condition of the lattice, [(+)(−)=constant at a constant temperature for an ionic solid where (+) and (−)

represent the cation and anion vacancy concentrations respectively] which contributes to the higher rate of decomposition [19–21].

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