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Effect of Ba^{2+} doping on the thermal decomposition of caesium bromate

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Abstract

The effect of Ba^{2+} doping on the isothermal decomposition of caesium bromate has been investigated in the range 633–673 K. It is observed that doping plays an important role in the thermal decomposition of caesium bromate which is immune to decomposition in its pure state. There is an initial rapid evolution of gas representing 1–2% of the reaction. The other stages through which decomposition proceeds are the acceleratory and decay stages. The presence of two decay stages (one short and one long) is indicated in the doped substance; the short decay stage diminishes with increase in temperature and is virtually absent at 673 K. The data over the entire sigmoidal regime are best fitted to a power law model, where the energies of activation of the decay stages are higher than that of the acceleratory stage. Microscopic observation reveals that the reaction begins essentially on the surface with the rapid formation of an interface and is followed by the penetration of the interface into the crystallite. The melting of a eutectic plays an important role in enhancing the decomposition rate.

INTRODUCTION

The decomposition of inorganic molecular ions has been studied in depth [1–7]. The decomposition can proceed in a solid state [8,9] or in a molten/semi-molten state due to formation of a eutectic between the solid product phase and the host material. Though the reaction in the solid state has received much attention, that in the molten/semi-molten [10,11] state has been neglected until now. The thermal decomposition of caesium bromate has not, to our knowledge, been previously investigated. Therefore, it is of interest to study the thermal decomposition of pure caesium

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bromate and Ba^{2+}-doped ceasium bromate, which undergoes decomposition through the formation a eutectic. Because pure caesium bromate does not decompose under the present conditions of study, our discussion is mainly concerned with doped caesium bromate.

EXPERIMENTAL

The caesium bromate was prepared from CsCl using the procedure of Boyd and Vaslow [12] and was purified by repeated recrystallisation. Doped (Ba^{2+}, 0.50 mol.%) crystals of caesium bromate were prepared by the procedure described earlier [4] and their uniformity was checked by chemical analysis as well as by X-ray diffraction studies. Isothermal kinetic studies of pure and doped caesium bromate decomposition were made through measurement [13] of the pressure of gas evolved in a constant volume pre-evacuated glass apparatus between 633 and 673 K. The fraction decomposed α (p/p_f) was calculated from the pressure values where p is the pressure at any time t and p_f is the pressure on complete decomposition.

RESULTS

The α–t curves for the isothermal decomposition of pure and doped crystals in the temperature range 633–673 K are represented in Fig. 1.

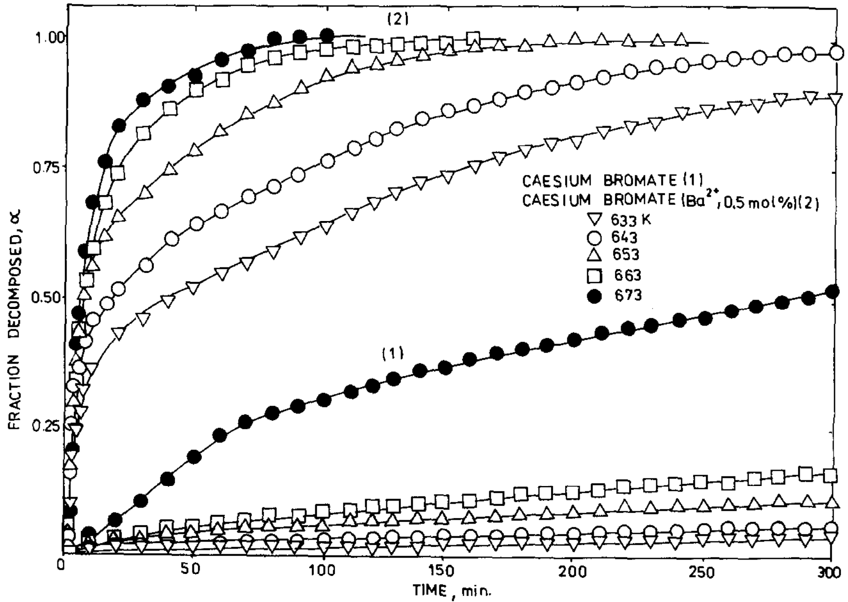

Fig. 1. Effect of temperature on the isothermal decomposition of pure and doped (Ba^{2+}, 0.50 mol.%) caesium bromate.

TABLE 1

Effect of temperature on α values (at 40 min of heating) of the thermal decomposition of pure and doped caesium bromate

Temp. (K)	633	643	653	663	673
Pure	0.016	0.018	0.034	0.048	0.146
Doped	0.488	0.592	0.748	0.861	0.901

Isothermal α versus time curves (633–673 K) of pure caesium bromate (Fig. 1) are predominantly deceleratory and those of doped caesium bromate are acceleratory, with no induction period, representing an initial rapid gas evolution comprising 1–2% of reaction. The other stages exhibited by the process are the acceleratory and decay stages, which are distinguished from each other by a discontinuity. The α value corresponding to the discontinuity α_d increases slightly with increase in temperature from 0.41 at 643 K to 0.46 at 673 K, the discontinuity at the same time being less prominent at higher temperatures. The presence of one short and one long decay stage is indicated in the α–t isotherms of doped caesium bromate; the short decay diminishes gradually with increase in temperature and is virtually absent at 673 K. The decomposition is en-

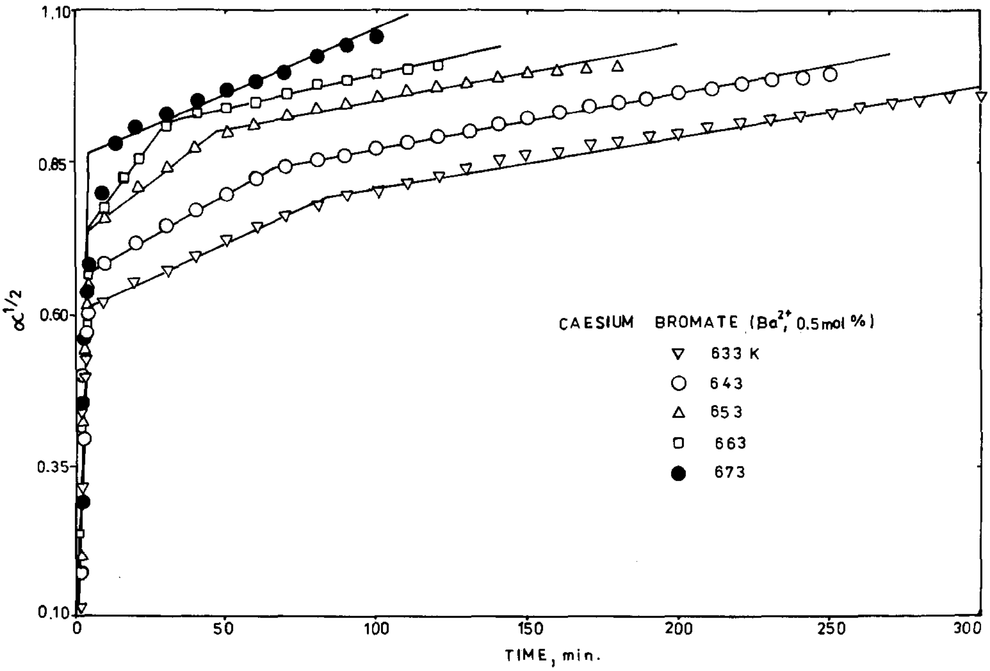

Fig. 2. Power law analysis of the kinetics of thermal decomposition of doped (Ba^{2+}, 0.50 mol.%) caesium bromate.

TABLE 2

Effect of temperature on the rate constants (10^2 min^{-1}) of doped (Ba^{2+}, 0.50 mol.%) caesium bromate

Temp. (K)	k_1 [a]	k_2 [b]	k_3 [b]
633	8.00	0.20	0.08
643	16.70	0.30	0.09
653	18.30	0.40	0.09
663	20.00	0.70	0.10
673	27.50	–	0.20
E (kJ mol^{-1})	110.62	138.02	128.97

[a] k_1, Power law rate constant for acceleratory period.

[b] k_2 and k_3, Power law constants for short decay and long decay respectively.

hanced at higher temperatures. The values of α for 40 min of heating at different temperatures are given in Table 1. The kinetic data obey the Power law equation [14] (Fig. 2)

$$\alpha^{1/2} = k_{1,2,3}t + C_1 \tag{1}$$

where $k_{1,2,3}$ are the rate constants and C_1 is the constant term. It is seen (Table 2) that the acceleratory rate constants are higher than those of both the decay rate constants and that the decay stages have higher activation energies than that of the acceleratory stage.

DISCUSSION

The most significant observation which must now be incorporated into the formulation of the reaction mechanism, is the formation of a eutectic [15]. The formulation of the reaction mechanism requires that the interpretation of the kinetic data is supported by microscopic observations and analytical measurements for the molten/semi-molten decomposed reactant. The discussion will be concerned with the two complementary aspects of the behaviour that require consideration in the formulation of the reaction mechanism of a molten/semi-molten state reaction: the reaction geometry and the chemistry of the changes occurring within the reaction zone.

The phase diagram of the system $CsBr/CsBrO_3$ is not known, but eutectic formation is very likely on chemical grounds and the occurrence of melting at temperatures well below the normal melting point (693 K) is perhaps the key to many unusual features.

The absence of an induction period suggests that $CsBrO_3$ decomposition belongs to that class of decomposition in which nucleation is rapid over the whole surface [16]. This is supported by the fact that the reaction is rapid in the early stages and by microscopic observations, in which the crystals were observed to become opaque which might be expected if the surface were covered by reaction products. Rapid decomposition and extensive cracking occur along sub-grain boundaries and other imperfections. Cracking may also account for the opaque nature of the crystals. The smallest crystals are the first to decompose completely. Therefore, the overall rate is proportional to the number of crystals remaining. The initial gas evolution is due to the release of occluded gases when the crystals break up on heating.

The discontinuity [15] is the result of the onset of melting. The product of the reaction, CsBr, probably forms a eutectic with $CsBrO_3$, lowering the thermodynamic melting point. This is detected visually under a hot-stage vacuum microscope. The melting here is different from ordinary melting and is dependent on the presence of CsBr, the amount of which is determined by the decomposition. Thus the two processes, melting of the eutectic and decomposition, are linked to each other in a complex manner.

During the initial heating (approx. 10 min), about 90% of the total gas yield was evolved in a rapid reaction. The enhanced initial reaction and the rate of the main reaction can be explained as follows. It is believed that melting plays an important role in the decomposition. Bromide ions formed by spontaneous decomposition at the surface have a certain mobility and are capable of catalysing the decomposition. Thus, in formulating a detailed reaction mechanism, we conclude, therefore, that the main reaction is an autocatalytic process in which the decomposition is promoted by Br^- ions, possibly associated with reactant mobility in the vicinity of the interface. The formation of CsBr around the host crystal introduces strain which contributes to the formation of cracks. In the intermediate temperature range, diffusion of reaction products into the crystal becomes fast enough for eutectic formation. The melting is complete in the high temperature region. It may be noted that the melting proposed here depends on eutectic formation which is a function of decomposition and diffusion. Therefore at this point it may be noted that the lower activation energy in the acceleratory region may result [15] from an energetically favourable reaction at the liquid/solid interface which, of course, disappears on complete melting.

ROLE OF DOPING

The cationic vacancies generated in the lattice of $CsBrO_3$ by doping with Ba^{2+} ion generate free space and local strain [8,11,17,18] which facilitate melting, consequently favouring decomposition. The strain distorts the structure of the crystal and alters the frequency of phonon vibration in the lattice. The relaxation time also changes in the region of the lattice surrounding the defect and a decrease in the symmetry of the bromate ion occurs. These factors facilitate melting, consequently favouring the decomposition.

The decomposition [19] of $CsBrO_3$ occurs as follows

$$2CsBrO_3 \rightarrow 2CsBr + 3O_2 \quad (2)$$

The intermediate species generated during the process are

$$BrO_3^- \rightsquigarrow BrO_3^{-*} \rightarrow BrO_2^- + O_2 \quad (3)$$

$$BrO_2^- \rightarrow BrO^- + O \quad (4)$$

$$BrO^- \rightarrow Br^- + O \quad (5)$$

$$O + O + Br^- \rightarrow Br^- + O_2 \quad (6)$$

The Br^- ions thus formed, together with certain types of impurities, act as electron donors [5,20] attracting oxygen atoms from neighbouring bromate ions giving rise to the intermediates BrO_2^- and BrO^-

$$BrO_3^- + Br^- \rightarrow BrO_2^- + BrO^- \quad (7)$$

The resulting bromite or hypobromite may decompose almost instantaneously

$$BrO_2^- \rightarrow Br^- + O_2 \quad (8)$$

$$BrO_3^- + BrO^- \rightarrow 2BrO_2^- \quad (9)$$

to give final products, or they may attract other oxygen atoms from neighbouring bromate ions. This type of reaction [21] may proceed through the reactant matrix and a stream of oxygen atoms would flow from the interior to the surface along a line of bromide ions, resulting in a rapid decomposition.

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REFERENCES

1 P.W.M. Jacobs and W.L. Ng, J. Solid State Chem., 9 (1974) 313.
2 S.D. Bhattamishra and S.R. Mohanty, Radiat. Effects, 29 (1976) 41.
3 D.J. Devlin and P.J. Herley, Thermochim. Acta, 104 (1986) 159.
4 D. Bhatta, B. Jena and (the late) S.R. Mohanty, Indian J. Chem., 27A (1988) 661.
5 D. Bhatta, M.K. Sahoo and B. Jena, J. Therm. Anal., 35 (1989) 1621.
6 D. Bhatta, M.K. Sahoo and B. Jena, Thermochim. Acta, 132 (1988) 7.
7 D. Bhatta, M.K. Sahoo and S. Mishra, Thermochim. Acta, 180 (1991) 155.
8 V.R. Paiverneker and K. Rajeshwar, J. Phys. Chem. Solids, 37 (1976) 67.
9 D.J. Devlin and P.J. Harley, Thermochim. Acta, 104 (1986) 159.
10 J. Jach, in J.H.D. Boer (Ed.), Proc. 4th Int. Symp. Reactivity of Solids, Elsevier, Amsterdam, 1960, p. 334.
11 B. Jena, S.R. Mohanty and M. Satapathy, Indian J. Chem., 19A (1980) 1139.
12 G.E. Boyd and F. Vaslow, J. Chem. Phys. Eng. Data, 7 (1962) 737.

13 S.D. Bhattamishra and S.R. Mohanty, J. Inorg. Nucl. Chem., 39 (1977) 2103.
14 D.A. Young, Decomposition of Solids, Pergamon, Oxford, 1966.
15 Mihir K. Sahoo and D. Bhatta, Radiat. Phys. Chem., in press.
16 W.E. Garner, Chemistry of the Solid State, Butterworths, London, 1955, Chapt. 7.
17 J.N. Maycok and V.R. Paiverneker, Proc. R. Soc. London Ser. A, 307 (1968) 303.
18 B.M. Mohapatra and D. Bhatta, Radiat. Phys. Chem., 27 (1986) 339.
19 J.A. Dean (Ed), Langes Handbook of Chemistry, 2nd edn., McGraw-Hill, New York, 1973.
20 F.R. Duke and E.A. Shute, J. Phys. Chem., 66 (1962) 2114.
21 D. Bhatta and M.K. Sahoo, Radiat. Eff. Defect Solids, 115 (1990) 113.