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ROLE OF γ-IRRADIATION AND Ba^{2+} DOPING ON THE ISOTHERMAL DECOMPOSITION OF CAESIUM BROMATE

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Role of γ-irradiation and Ba^{2+} doping on the isothermal decomposition of caesium bromate has been investigated gasometrically. It is seen that decomposition proceeds in a molten/semi-molten state presumably due to formation of an eutectic between the product bromide and the host material, i.e., bromate. The process exhibits stages: (i) initial gas evolution (initial puff) (ii) short acceleratory and (iii) long decay. The data are analysed in the light of theories of different kinetic models like Prout-Tompkins, Avrami-Erofeev and explore that irradiation as well as doping enhance decomposition.

Introduction

Although decomposition of many inorganic molecular ions and the role of cation/anion doping and γ-irradiation on the process has been well studied [1–6], substances which decompose in a molten/partial-molten state have not received much attention. The surfaces of sodium and potassium [7, 8] bromates become completely covered with a layer of product bromide right from the beginning of the decomposition which subsequently proceeds by an advance into the crystal of the interface, generated between the undecomposed bromate and the product bromide. The eutectic, thus formed lowers the melting point of the substance, as a result of which it melts below the thermo-dynamic melting point. The present study relates to the influence of γ-irradiation (4.0 MGy) and cation doping (Ba^{2+}) on the isothermal decomposition of caesium bromate which proceeds in a molten/semi-molten state.

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Experimental

Caesium bromate was prepared from caesium chloride by adopting the procedure of Boyd and Vaslow [9] and was purified by repeated crystallization. Doped crystals of caesium bromate with Ba^{2+} ions (0.5 mol%) were prepared from a solution of the corresponding salts by coprecipitation method and were characterized by chemical analysis as well as by X-ray diffraction study. The material was exposed to 4.0 MGy of ^{60}Co γ-rays at the dose rate of 0.24×10^{-2} MGy h^{-1} and decomposition study was carried out at 673 K gasometrically [2, 5] using vacuum apparatus. The fractional decomposition, α ($=p/p_f$) was calculated from pressure values.

Results and discussion

Caesium bromate begins to decompose at 538 K and melts with decomposition [10] at 693 K as

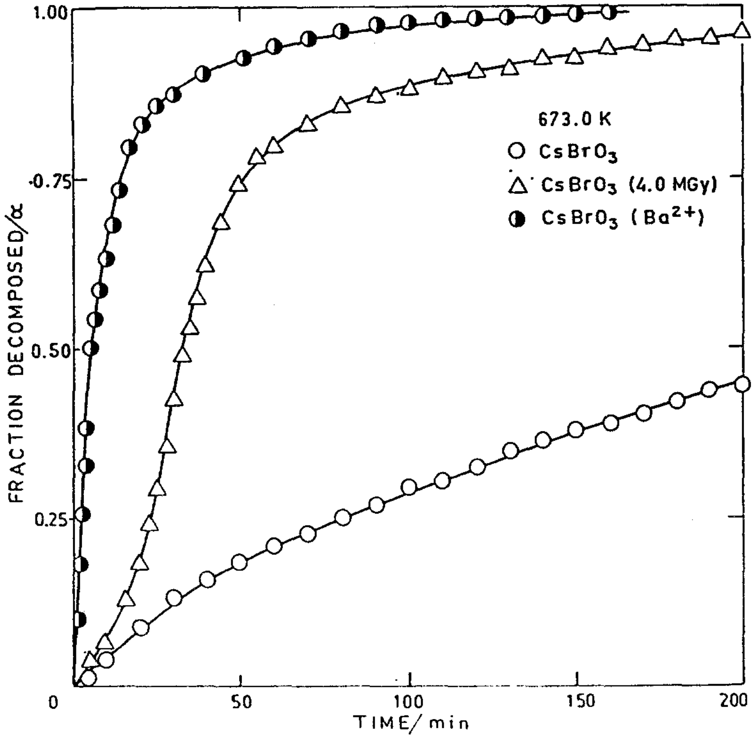

Fig. 1 Isothermal decomposition of pure, irrad. and doped caesium bromate at 673.0 K

$$2CsBrO_3 \rightarrow 2CsBr + 3O_2 \qquad (1)$$

The $\alpha - t$ plots (Fig. 1) are sigmoidal in nature with small amount of initial gas evolution ($\alpha \sim 0.04$) which is possibly due to release of occluded air present at the crystal surface. The liberation of gas is completed within first few minutes of heating and remains unaffected either by irradiation or by doping. Absence of induction period as well as linear stage suggests that probably the surfaces of normal, irradiated and doped crystals are nucleated [7, 11] instantaneously followed by some form of Prout-Tompkins [12] and Avrami-Erofeev [13] relationships. During decomposition of caesium bromate, the surfaces of the crystals are plausibly covered with a layer of product bromide (CsBr) right from the beginning of the decomposition which subsequently proceeds into the crystal of the interface, generated between the undecomposed bromate and the product bromide. The simultaneous presence of these two species results eutectic, hence the substance melts below its thermodynamic melting point (693 K), which has been

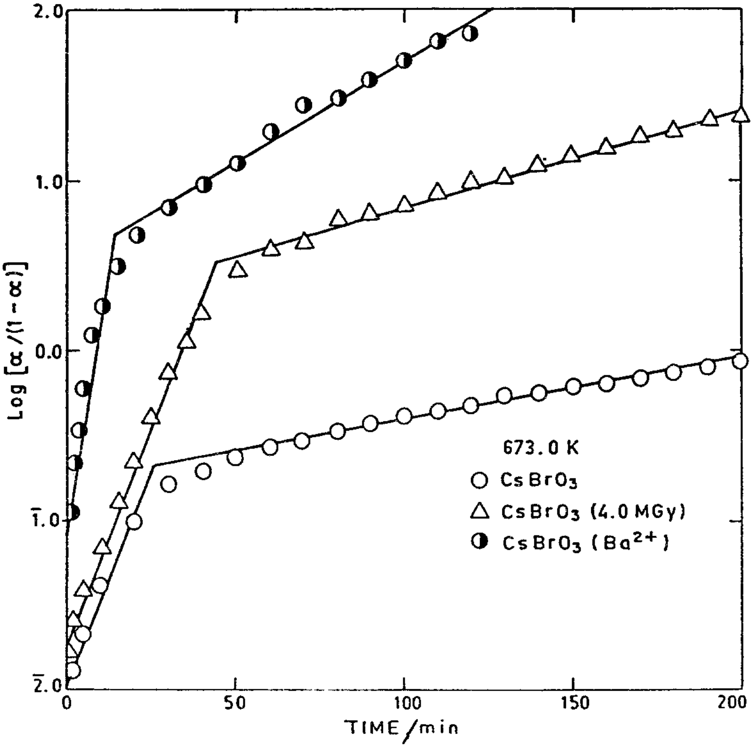

Fig. 2 Prout-Tompkins analysis of the kinetics of isothermal decomposition of pure, irrad. and doped caesium bromate

detected visually under a hot-stage vacuum microscope. The process in the present study is controlled by two rate constants, i.e., melting of a eutectic mixture and its decomposition, which are interrelated to one another. So factors, which result enhance melting will favour decomposition.

The data are analysed according to Prout-Tompkins [12] mechanism (Fig. 2).

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

and Avrami-Erofeev [13] relationship (Fig. 3) with $n = 2$ and $n = 3$

$$[-\log(1-\alpha)]^{1/n} = k_{3,4}t + C_2 \qquad (3)$$

where k_1, k_3 and k_2, k_4 are respectively the rate constants for the acceleratory and decay stages, C_1 and C_2 are constants. The ranges of applicability of Eqs (2) and (3) over the entire sigmoidal zone being $0.02<\alpha<0.46$ (Normal), $0.04<\alpha<0.96$ (Irrad.) and $0.09<\alpha<0.98$ (Doped). It is evident from Table 1 that the rate constant of the acceleratory stage remains unaffected by irradiation but is facilitated by doping whereas that of the decay period is enhanced by both these treatments.

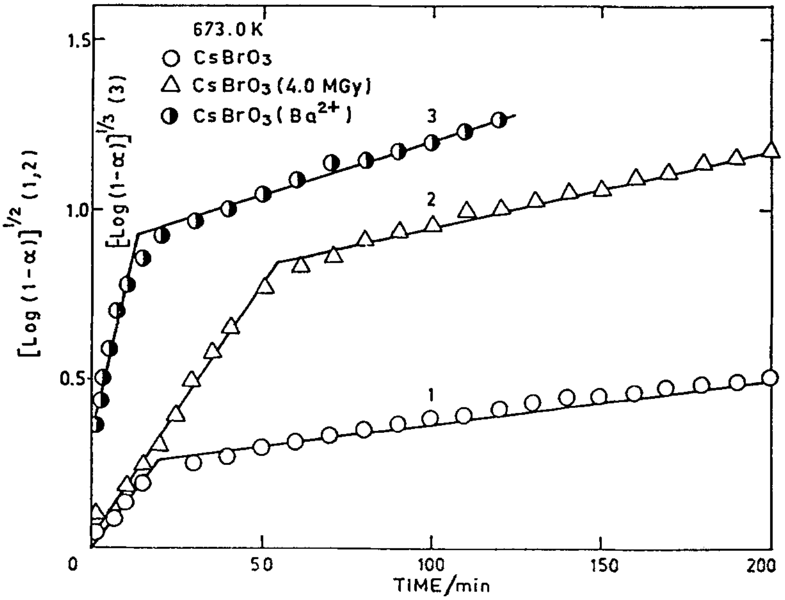

Fig. 3 Avrami-Erofeev analysis of the kinetics of thermal decomposition of pure, irrad. and doped caesium bromate

Table 1 Temperature dependence of velocity constants in the thermal decomposition of pure, irrad. (4.0 MGy) and doped (Ba^{2+}) caesium bromate at 673.0 K

Substance	Prout-Tompkins		Avrami-Erofeev	
	k_1	k_2	k_3	k_4
Pure	6.0	0.37	1.6	0.13
Irrad.	6.6	0.57	1.7	0.22
Doped	13.0	1.2	3.7	0.32

$k_1 - k_4 / 10^2$, min^{-1}

The reaction in the acceleratory period takes place due to strain exerted by the growing nuclei and the autocatalytic effect [5, 6] of the solid product phase, CsBr which occurs homogeneously [7] throughout the reacting mass thereafter. Also the evolved oxygen easily escapes [14] from the melt collecting other oxygen molecules in its path contributing to higher decomposition rate indicating that nucleation occurs in a chain branching manner.

The decay period plausibly occurs at the point where resolidification starts with separation of solid product, caesium bromide from the eutectic mixture. Though bromide generated in the beginning of the reaction, catalyse [15] the decomposition, after certain time interval when appreciable amount of the former is deposited results decelaration. The former phenomenon may be attributed to catalytic effect whereas the later to cage effect, i.e., CsBr, deposited over the caesium bromate crystals act as a barrier for the further decomposition to proceed. Data on pure, irradiated and doped crystals are well analysed in the light of theory of Prout-Tompkins [12] relationship and Avrami-Erofeev mechanism [13] exploring that nucleation occurs in a chain branching manner and there are two ($n = 2$, pure and irrad.) and three ($n = 3$, doped) dimensional growth of nuclei.

Role of irradiation

Upon irradiation of caesium bromate with ^{60}Co γ-rays, the BrO_3^- ion undergoes excitation and ionization leading to rupture of the bromine-oxygen bonds. The entities generated [16] are mainly; Br^-, BrO^-, BrO_2^-, O_3^-, O_2 and BrO_4^- and play an important role both in nucleation and nuclei growth [2, 4]. Irradiated crystals when subjected to thermal decomposition, the bromine bearing species undergo decomposition resulting bromide and O_2 in the manner discussed earlier [5, 6].

As the decomposition in the present case proceeds in a molten/partial-molten state, radiation induced lattice defects and trapped charges no longer exist [8] and the observed effects due only to the chemical damage fragments generated upon irradiation which constitute decomposition nuclei themselves and may be termed as irradiation nuclei [14, 17]. Irradiation influences decomposition which may arise due to enhance melting rate and also increased penetration (or growth) rate. Melting precedes decomposition [18] and since irradiation will not affect the liquid state, it is safe to assume an enhance melting rate which is plausibly associated with the strain brought about by the irradiation decomposition products, i.e., CsBr and O_2. The present data are in agreement with the theory that melting is facilitated by irradiation and is continued for a longer period (duration of the acceleratory stage), resulting higher decomposition.

Role of doping

Incorporation of a divalent ion, Ba^{2+} into the crystal lattice of caesium bromate generates cationic vacancy resulting free space and local strain [19-21]. The strain so generated distorts the structure of the crystal and alters the frequency of the 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 ions occurs. These factors [22] substantially weaken the 'Br–O' bond in the vicinity of the defects thus increasing the reactivity of the solid. The extent of decomposition is higher in the case of doped crystals than that of the pure and irradiated salts which may be ascribed to higher melting rate, resulted due to cationic vacancy [23]. The formation of solid product phase, CsBr increased with increasing time of heating and when sufficient amount of it is deposited resolidification starts earlier causing deceleration.

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References

1 P. W. M. Jacobs and Y. W. L. Ng, J. Solid State Chem., 9 (1974) 315.
2 S. D. Bhattamishra and S. R. Mohanty, Radiat. Effect., 29 (1976) 41.

3 D. J. Devlin and P. J. Harley, Thermochim. Acta, 104 (1986) 159.
4 N. Bohidar, B. Jena and S. R. Mohanty, J. Radioanalyt. Nucl. Chem. Letters, 95 (1985) 291.
5a D. Bhatta, M. K. Sahoo and B. Jena, Thermochim. Acta 132 (1988) 7.
5b D. Bhatta, Ms. S. Mishra and M. K. Sahoo, Thermochim. Acta, (1990).
6 D. Bhatta, B. Jena and S. R. Mohanty (Late), Indian J. Chem., 27A (1988) 661.
7 J. Jach, Proc. 4th International Symposium on the Reactivity of Solids (Ed. J. H. De Boer) Elsevier, Amsterdam 1960, p. 334.
8 J. Jach, J. Phys. Chem. Solids, 24 (1963) 63.
9 G. E. Boyd and F. Vaslow, J. Chem. Phys. Eng. Data., 7 (1962) 237.
10 J. A. Dean (Ed.), Langes Handbook of Chemistry, 2nd ed., McGraw-Hill Book Co. Inc., New York 1973.
11 P. J. Harley and E. G. Prout, J. Phys. Chem., 64 (1970) 675.
12 E. G. Prout and F. C. Tompkins, Trans. Faraday Soc., 40 (1944) 468.
13 B. V. Erofeev, Compt. Rend. Acad. Sci. U.R.S.S., 52 (1946) 511.
14 N. Bohidar and S. R. Mohanty, Radiochim. Acta, 27 (1980) 19.
15 D. Bhatta, M. K. Sahoo and B. Jena, J. Thermal Anal., 35 (1989) 1619.
16 D. Bhatta, S. R. Mohanty and K. C. Samantaray, Radiochim. Acta, 28 (1981) 13.
17 E. G. Prout, National Conference on Nuclear Energy, Pretoria, 1963, p. 25.
18 A. K. Galwey, Chemistry of Solids, Chapman Hall, London 1967.
19 J. N. Maycock and V. R. Pai Verneker, Proc. Roy. Soc., A.307 (1968) 303.
20 V. R. P. Verneker and K. Rajeshwar, J. Phys. Chem. Solids, 37 (1976) 67.
21 B. M. Mohapatra and D. Bhatta, Radiat. Phys. Chem., 27 (1986) 339.
22 B. Jena, S. R. Mohanty and M. Satapathy, Indian J. Chem., 19A (1980) 1139.
23 D. Bhatta and M. K. Sahoo, Reactivity of Solids, in press.

Zusammenfassung — Mittels Gasometrie wurde die Rolle von Bestrahlung und Versetzen mit Ba^{2+} bei der isothermen Zersetzung von Cäsiumbromat untersucht. Es zeigte sich, daß die Zersetzung in einem geschmolzenen/semi-geschmolzenem Zustand erfolgt, wahrscheinlich infolge der Bildung eines Eutektikums zwischen dem Bromidprodukt und der Wirtssubstanz Bromat. Dieser Prozeß läuft in mehreren Schritten ab: (i) anfängliche Gasentwicklung, (ii) kurze Beschleunigung und (iii) langes Abklingen. Die Angaben wurden hinsichtlich von Theorien verschiedener kinetischer Modelle, wie z.B. Prout-Tompkins oder Avrami-Erofeev untersucht und zeigen, daß sowohl Bestrahlung als auch Versetzen die Zersetzung begünstigen.