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# Influence of trivalent ion dopants on the thermal decomposition kinetics of potassium bromate

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ABSTRACT

Isothermal decomposition of potassium bromate ($KBrO_3$) has been studied as a function of concentration of dopants, phosphate and aluminium by thermogravimetry (TG) in the temperatures range 668–683 K. The TG data were subjected to both model fitting and model free kinetic methods of analysis. The model fitting analysis shows that the decomposition of both pure and doped samples was best described by contracting cylinder equation, $[1-(1-\alpha)^{1/2} = kt]$ with two different rate constants $k_1$ (for $\alpha = 0.15$–$0.45$) and $k_2$ (for $\alpha = 0.5$–$0.95$) such that $k_1 < k_2$. The rate law remained unaltered by doping. Both $k_1$ and $k_2$ increases with increase in dopant concentration. The diffusion of ions, $K^+$ and $BrO_3^-$, is determining the rate in both stages. The formation of $KBr$–$KBrO_3$ eutectic and consequent melting is observed in the stage 2 process of the decomposition.



## 1. Introduction

Knowledge of the effects of pretreatments on the kinetics of solid state reactions provides a deep insight not only into the topochemistry but also into the mechanism and control of these reactions. With this view we have embarked on a systematic study of the effects of various pretreatments (doping, precompression, preheating, particle sizing, etc.) on the thermal behaviour of some technologically important high energy solids belonging to halates, perhalates, permanganates, azides, etc., and recently we have reported some interesting results [1–8].

Potassium bromate ($KBrO_3$) is a white crystalline powder, which is colourless, odourless, and tasteless with a molecular mass of 167 g. $KBrO_3$ has no medicinal value but is added to fish paste as a conditioner, and also to beer or cheese [9] and has also been used as a constituent in cold wave hair solution [10]. $KBrO_3$ may be fatal if swallowed, harmful if inhaled or absorbed through skin and causes irritation to skin, eyes, respiratory tract and kidney damage.

### 1.1. Thermoanalytical studies

Information about the thermal stability of solid materials of all kinds is of great practical and technological importance [11–13]. Thermogravimetric analysis (TG) is usually adopted to study the kinetics of thermally activated solid state reactions to obtain thermal stability parameters of solids [14–18]. The kinetics of the thermal decomposition of inorganic materials could be markedly affected by pre-treatments, by the shortening of the induction period followed by an overall decrease in time needed to complete the reaction. The thermal decomposition data generated from TG can be analyzed and manipulated to obtain kinetic parameters such as activation energy ($E$) and pre-exponential factor ($A$) [14–21]. Solid-state kinetic data are of practical interest for the large and growing number of technologically important processes. Kinetic studies predict how quickly a system approaches equilibrium and also help to understand the mechanism of the process [22,23]. A number of reviews are available in the literature on these processes [24–31]. Several authors have emphasized the practical and theoretical importance of information on the kinetics and mechanism of solid state decompositions [11,32–34].

The mass loss data obtained from thermogravimetric studies in the present study support the findings of Bancroft and Gesser [35] that the thermal decomposition reaction proceeds according to the equation:

$$2KBrO_3 \rightarrow 2KBr + 3O_2$$

Jach [36,37] reported that there is an initial rapid evolution of gas in the thermal decomposition of $KBrO_3$ (1–2% decomposition), which could be eliminated by grinding or irradiation. This initial stage was followed by an exponential decay reaction in the temperature range 615–640 K. At higher temperatures (652–685 K) he

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**Table 1**
Different reaction models used to describe the reaction kinetics.

| Model No. | Reaction model | Function, $g(\alpha)$ |
|---|---|---|
| 1 | Power law | $\alpha^{1/4}$ |
| 2 | Power law | $\alpha^{1/3}$ |
| 3 | Power law | $\alpha^{1/2}$ |
| 4 | Power law | $\alpha^{3/2}$ |
| 5 | Exponential law | $\ln\alpha$ |
| 6 | One-dimensional diffusion | $\alpha^2$ |
| 7 | Mampel (first order) | $-\ln(1-\alpha)$ |
| 8 | Avrami–Erofeev | $[-\ln(1-\alpha)]^{1/4}$ |
| 9 | Avrami–Erofeev | $[-\ln(1-\alpha)]^{1/3}$ |
| 10 | Avrami–Erofeev | $[-\ln(1-\alpha)]^{1/2}$ |
| 11 | Avrami–Erofeev | $[-\ln(1-\alpha)]^{3/4}$ |
| 12 | Avrami–Erofeev | $[-\ln(1-\alpha)]^{2/3}$ |
| 13 | Three-dimensional diffusion | $[1-(1-\alpha)^{1/3}]^2$ |
| 14 | Contracting sphere | $1-(1-\alpha)^{1/3}$ |
| 15 | Contracting cylinder | $1-(1-\alpha)^{1/2}$ |
| 16 | Contracting interface | $1-1-\alpha)^{2/3}$ |
| 17 | Second order | $(1-\alpha)^{-1}-1$ |
| 18 | Prout–Tompkins | $\ln[\alpha/(1-\alpha)]$ |

observed a short acceleratory process to precede the exponential decay. The activation energies of the acceleratory and decay processes were 171 and 221 kJ mol$^{-1}$, respectively. He proposed the formation of a eutectic between $KBrO_3$ and the product KBr in order to account for the observed melting of the solid well below the normal melting point, 707 K. According to derivatographic studies, the decomposition of $KBrO_3$ begins after melting; showing endotherms indicating melting at 400 °C and exotherms relating to decomposition at 430 C [38]. Breusov et al. [39] observed endotherms at 350 °C and exotherms at 405 °C in the differential thermal analysis (DTA) of $KBrO_3$. Solymosi [38] studied the decomposition of $KBrO_3$ in the temperature range 665–677 K and observed that the decomposition obeyed the Prout Tompkins [40] equation with separate rate constants and activation energies viz., 195 kJ mol$^{-1}$ ($\alpha$ = 0.04–0.46) and 173 kJ mol$^{-1}$ ($\alpha$ = 0.5–0.95). He also observed that the range $\alpha$ = 0.3–0.95 can be fitted to the first order rate equation with an activation energy of 191.6 kJ mol$^{-1}$. Diefallah et al. [41] followed the decomposition of $KBrO_3$ by isothermal as well as nonisothermal methods. They reported that under isothermal conditions the kinetics of the decomposition (in the temperature range 653–693 K) followed contracting sphere equation with activation energy of 193.3 kJ mol$^{-1}$.

Joseph et al. [42] investigated catalytic effect of metal oxide on the thermal decomposition of $KBrO_3$ and found that $Al_2O_3$ is almost as good a catalyst as any other oxide used unlike in the thermal decomposition of $KClO_3$. In the case of $TiO_2$ there was an increase in the activation energy of decomposition. The effects of admixtures of potassium bromide (2.5% and 5%) on the thermal decomposition of $KBrO_3$ were studied by Mohanty et al. [43], in the temperature range 653–683 K, and found that a three stage process; (i) initial gas evolution, (ii) acceleratory and (iii) decay steps occurs in the thermal decomposition. They analyzed the TG data on the basis of the first-order law with two rate constants $k_1$ and $k_2$, $k_1$ being the rate constant for the initial, slow first-order process ($\alpha$ = 0.02–0.26), and $k_2$ being the rate constant for the subsequent faster process in the range $\alpha$ = 0.21–0.98 and found that the range for the slow and faster processes became 0.01 to 0.16 and 0.1 to 0.98, respectively when the concentration of added potassium bromide is increased to 5%.

The isothermal decomposition of doped and normal $KBrO_3$ samples was carried out gasometrically between the temperature range 653–663 K and the results reveal that the process occurs through initial gas evolution, acceleratory and decay stages [44]. It has also been observed that doping enhances the rate of the reaction, the effect being more pronounced in the case of sulphate and the TG data were found to be well fitted to the Prout–Tompkins and Avrami–Erofe'ev mechanisms. It has been found, on survey of the literature, that no more studies on the thermal decomposition and kinetics of potassium bromate are reported in the literature.

Our earlier investigations showed that the isothermal decomposition of $KBrO_3$ proceeds through contracting cylinder model kinetics at all temperatures studied [2,7,8]. As a part of our study of the effect of various pretreatments on the thermal behaviour of high energy solids, we have examined the isothermal decomposition of $KBrO_3$ [2] as a function of small concentrations of the dopants, $SO_4^{2-}$ and $Ba^{2+}$, by isothermal thermogravimetry in the temperature range 668–683 K. The results suggested a diffusion-controlled mechanism for the decomposition of $KBrO_3$, the diffusing species being both $K^+$ and $BrO_3^-$. Pure and doped samples of $KBrO_3$ were subjected to precompression and their thermal decomposition kinetics was studied by TG at 668 K [7]. The samples decomposed in two stages governed by the same rate law (contracting cylinder equation), but with different rate constants, $k_1$ (for $\alpha \leq 0.45$) and $k_2$ (for $\alpha \geq 0.45$), as in the case of uncompressed samples. The rate constants $k_1$ and $k_2$ decreased dramatically on precompression, the decrease being higher for doped samples. Cation dopants ($Ba^{2+}$ and $Al^{3+}$) caused more desensitization effect than the anion dopants ($SO_4^{2-}$ and $PO_4^{3-}$) of the same magnitude of charge and concentration. The results favor ionic diffusion mechanism proposed earlier on the basis of doping studies [2]. The thermal decomposition of $KBrO_3$ has also been studied as a function of particle size, in the range 53–150 μm, by isothermal thermogravimetry at different temperatures, *viz.* 668, 673, 678 and 683 K in static air atmosphere [8]. Isothermal model fitting analysis shows that the thermal decomposition kinetics of all the samples of $KBrO_3$ studied follows the contracting cylinder equation. We observed a regular increase in rate of decomposition of $KBrO_3$ with reduction in particle size, which we suggest, is an impact of melting of this solid during decomposition.

The objective of this work is to investigate the effect of trivalent dopants, $PO_4^{3-}$ and $Al^{3+}$, on the thermal decomposition kinetics of $KBrO_3$ by isothermal thermogravimetry. In the present study great emphasis is given to reliable activation energy values for the forward reaction, $2KBrO_3 \rightarrow 2KBr + 3O_2$, which allows one to draw mechanistic conclusions as well as to predict the kinetics of the process.

## 2. Experimental

### 2.1. Materials

All the chemicals used in the present study were of AnalaR grade samples of E Merck. 8 g of $KBrO_3$ is dissolved in 360 cm$^3$ of distilled water at 331 ± 1 K. The solution was cooled slowly to room temperature, the resulting crystals of pure $KBrO_3$ were removed, air dried, powdered in an agate mortar, fixed the particle size in the range 106–125 μm and kept in a vacuum desiccator. Doped samples were prepared by following the above procedure for an aqueous solution (360 cm$^3$) containing 8 g of $KBrO_3$ and required proportion of the dopant. The dopants used were $K_3PO_4$ and $AlCl_3{\cdot}6H_2O$ at concentrations $10^{-4}$, $10^{-3}$, $10^{-2}$ and $10^{-1}$ mol%. As in earlier works, the concentration of the dopants refers to the solution from which they were crystallized. The crystals of all the doped samples were removed; air dried, powdered in an agate mortar, fixed the particle size in the range 106–125 μm and kept in a vacuum desiccator.

### 2.2. Methods

Thermogravimetric measurements in static air were carried out on a custom-made thermobalance fabricated in this laboratory