

## CATALYTIC EFFECTS OF LANTHANIDE OXIDES ON THE THERMAL DECOMPOSITION OF BARIUM PERCHLORATE

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### Abstract

Catalytic activities exerted by the lanthanide oxides  $\text{Ln}_2\text{O}_3$  ( $\text{Ln}=\text{La, Sm, Gd and Dy}$ ) (0.25 mol%) on the thermal decomposition of barium perchlorate were studied gasometrically at 718 K. The  $\alpha$  vs.  $t$  plot for the salt alone displays (i) initial gas evolution (ii) an induction period, (iii) a short acceleratory stage and (iv) a long decay stage. For the mixtures with  $\text{Ln}_2\text{O}_3$ , phenomena (i) and (ii) are not observed.  $\text{Ln}_2\text{O}_3$  enhances the rate of reaction in both the acceleratory and the decay stage, and increases the fraction decomposed,  $\alpha$ , in the sequence  $\text{La}_2\text{O}_3 > \text{Gd}_2\text{O}_3 > \text{Sm}_2\text{O}_3 > \text{Dy}_2\text{O}_3$ .

The influence of  $\text{Dy}_2\text{O}_3$  (0.25–2.0 mol%) on the decomposition of  $\text{Ba}(\text{ClO}_4)_2$  at 718 K indicates that such admixture facilitates the process and the effect increases with increasing concentration.

The salt alone and the mixtures decompose through the same stages in the temperature range 703–733 K as at 718 K. The data on both types of samples fit well to the Prout–Tompkins and the Avrami–Erofeev mechanism, suggesting that nucleation takes place in a chain-branching manner and that the two-dimensional growth of the nuclei occurs during the process. Admixture enhances the rate of reaction marked without affecting the energy of activation.

**Keywords:** barium perchlorate, catalytic effect, lanthanide oxides

### Introduction

In consequence of their high oxygen content, perchlorates find applications as oxidants in propellants, explosives and pyrotechnic compositions [1]. The mechanical addition of foreign substances to metallic salts can bring about significant changes [2–4] in the topochemical reaction behaviour of these materials; these changes may be due to (i) the catalytic effect of the admixture, which accelerates or decelerates the reaction, or (ii) a chemical reaction between the reactant and the admixture, giving rise to new substances. Kinetic studies of the decomposition of such materials are needed to provide detailed knowledge of the behaviour and mechanistic criteria of the reactions.

$\text{Ln}_2\text{O}_3$ , important constituents of high- $T_c$  superconductors, are basic in nature [5] and act as  $p$ -type semiconductors [6]. In these compounds, the electrons present in the

4f level are responsible for a wide range of physicochemical properties. The present study is an attempt to evaluate the thermochemical data on the decomposition of  $\text{Ba}(\text{ClO}_4)_2$  mixed with different concentrations of  $\text{Ln}_2\text{O}_3$ , in order to ascertain their catalytic activity and the mechanism involved.

## Experimental

Crystals of barium perchlorate trihydrate (AR grade) were dehydrated at 523 K and physical mixtures of the anhydrous salt with 0.25 mol% of  $\text{Ln}_2\text{O}_3$  ( $\text{Ln}=\text{La}$ , Sm, Gd and Dy) were prepared by mixing the required amounts of the salt and the oxide and grinding thoroughly in an agate mortar. Solid solutions of  $\text{Ba}(\text{ClO}_4)_2$  with  $\text{Dy}_2\text{O}_3$  of different concentrations (0.25–2.0 mol%) were prepared by the same procedure, and the decompositions of the salt alone and its mixtures were studied gasometrically at 718 K [7].

$\text{Ba}(\text{ClO}_4)_2$  and  $\text{Ba}(\text{ClO}_4)_2+\text{Dy}_2\text{O}_3$  mixtures were decomposed in the temperature range 703–733 K; in all cases, the fraction decomposed,  $\alpha$ , was calculated from the pressure values  $p/p_t$ , where  $p$  is the pressure at time  $t$  and  $p_t$  is the final pressure on completion of the reaction.

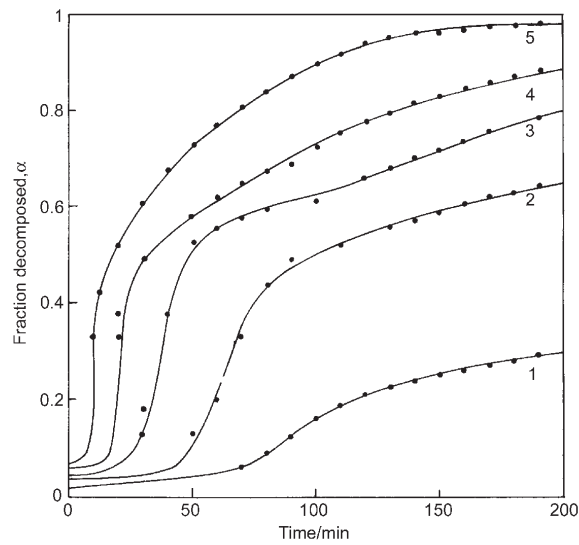
## Results and discussion

The decomposition isotherms of the salt alone (Fig. 1) and of its mixtures (Fig. 2) indicate that the decomposition of  $\text{Ba}(\text{ClO}_4)_2$  alone exhibits (i) initial gas evolution, (ii) an induction period, (iii) a short acceleratory stage and (iv) a long decay stage, whereas for the mixtures with  $\text{Ln}_2\text{O}_3$ , phenomena (i) and (ii) are not observed. The process occurs with an acceleratory period at the beginning of the decomposition for the mixtures. Values of  $\alpha$  for different time intervals are given in Table 1.

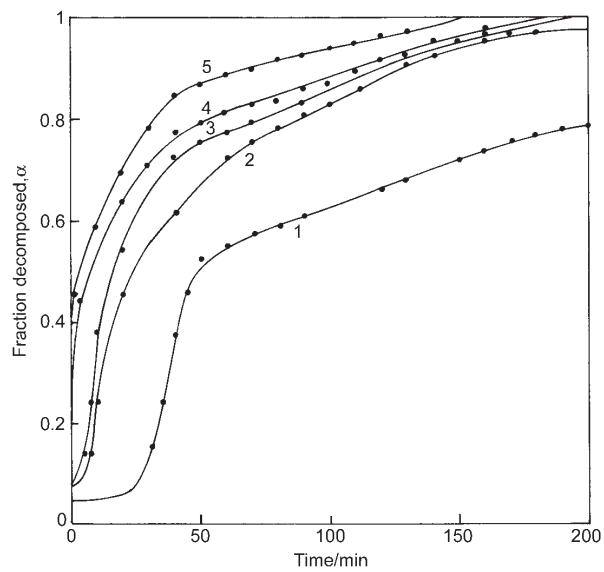
**Table 1** Values of fractional decomposition  $\alpha$  for  $\text{Ba}(\text{ClO}_4)_2$  and for  $\text{Ba}(\text{ClO}_4)_2+\text{Ln}_2\text{O}_3$  mixtures after different time intervals

Mixture	Time/min			
	20	40	60	100
$\text{Ba}(\text{ClO}_4)_2$ (alone)	0.06	0.38	0.56	0.62
$\text{Ba}(\text{ClO}_4)_2+\text{La}_2\text{O}_3$	0.70	0.85	0.89	0.95
$\text{Ba}(\text{ClO}_4)_2+\text{Gd}_2\text{O}_3$	0.65	0.78	0.82	0.87
$\text{Ba}(\text{ClO}_4)_2+\text{Sm}_2\text{O}_3$	0.55	0.75	0.78	0.86
$\text{Ba}(\text{ClO}_4)_2+\text{Dy}_2\text{O}_3$	0.49	0.68	0.78	0.83

It is evident from the data that  $\text{Ln}_2\text{O}_3$  enhances the reaction, the effect being more marked in the initial period and gradually decreasing with increasing duration of heating. There is a 10-fold increase in the value of  $\alpha$  after 20 min of heating, which decreases to 1.5-fold at 100 min for the  $\text{Ln}_2\text{O}_3$  admixture, and the catalyst is so effective that ~90.9% of decomposition has taken place by 40 min of heating. The catalytic activity of  $\text{Ln}_2\text{O}_3$  follows the sequence  $\text{La}_2\text{O}_3>\text{Gd}_2\text{O}_3>\text{Sm}_2\text{O}_3>\text{Dy}_2\text{O}_3$ .



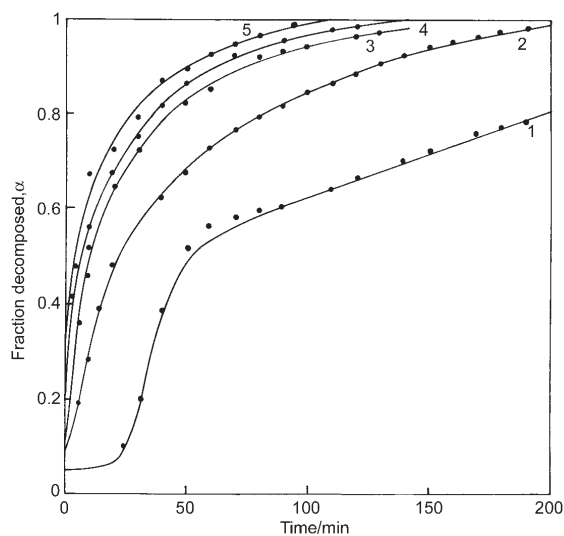
**Fig. 1** Thermal decomposition of barium perchlorate alone at different temperatures



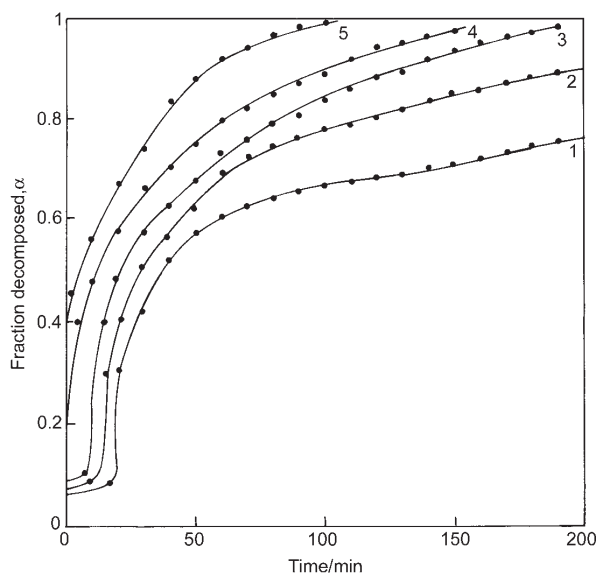
**Fig. 2** Thermal decomposition of 1 –  $\text{Ba}(\text{ClO}_4)_2 + \text{Ln}_2\text{O}_3$  mixtures at 718 K ( $\text{Ln} = \text{La}, \text{Sm}, \text{Gd}$  and  $\text{Dy}$  with 0.25 mol%) 2 –  $\text{Ba}(\text{ClO}_4)_2 + \text{Dy}_2\text{O}_3$ ; 3 –  $\text{Ba}(\text{ClO}_4)_2 + \text{Sm}_2\text{O}_3$ ; 4 –  $\text{Ba}(\text{ClO}_4)_2 + \text{Gd}_2\text{O}_3$ ; 5 –  $\text{Ba}(\text{ClO}_4)_2 + \text{La}_2\text{O}_3$

The decomposition data on  $\text{Ba}(\text{ClO}_4)_2 + \text{Dy}_2\text{O}_3$  mixtures (0.25–2.0 mol%) at 718 K, presented in Fig. 3, suggest that the reaction is instantaneous at the beginning

of the acceleratory period and subsequently undergoes a decay stage. Values of  $\alpha$  for different time intervals are recorded in Table 2.



**Fig. 3** Thermal decomposition of 1 –  $\text{Ba}(\text{ClO}_4)_2 + \text{Dy}_2\text{O}_3$  (0.25–2.0 mol%) mixtures at 718 K; 2 –  $\text{Ba}(\text{ClO}_4)_2 + 0.25$  mol%  $\text{Dy}_2\text{O}_3$ ; 3 –  $\text{Ba}(\text{ClO}_4)_2 + 0.5$  mol%  $\text{Dy}_2\text{O}_3$ ; 4 –  $\text{Ba}(\text{ClO}_4)_2 + 0.75$  mol%  $\text{Dy}_2\text{O}_3$ ; 5 –  $\text{Ba}(\text{ClO}_4)_2 + 1.00$  mol%  $\text{Dy}_2\text{O}_3$ ;



**Fig. 4** Thermal decomposition of  $\text{Ba}(\text{ClO}_4)_2 + \text{Dy}_2\text{O}_3$  (0.25 mol%) mixture at different temperatures; 1 – 703 K; 2 – 708 K; 3 – 718 K; 4 – 723 K; 5 – 733 K

**Table 2** Values of fractional decomposition  $\alpha$  for  $\text{Ba}(\text{ClO}_4)_2$  and for  $\text{Ba}(\text{ClO}_4)_2+\text{Dy}_2\text{O}_3$  mixtures after different time intervals

Dy <sub>2</sub> O <sub>3</sub> content/ mol%	Time/min				
	20	60	100	140	180
0	0.06	0.56	0.62	0.70	0.77
0.25	0.49	0.73	0.83	0.94	0.97
0.50	0.65	0.85	0.94	0.98	–
1.00	0.67	0.90	0.97	–	–
2.00	0.72	0.92	0.99	–	–

It is seen that  $\alpha$  increases with increasing concentration of oxide and with increasing duration of heating. The highest concentration (2.0 mol%) catalyses the process to such an extent that the reaction is almost complete (~99%) after 100 min of heating. A similar trend in the decomposition pattern, i.e. a long acceleratory stage and a short decay stage, is observed in this case as for the other  $\text{Ln}_2\text{O}_3$ .

The decomposition isotherms of  $\text{Ba}(\text{ClO}_4)_2$  and the  $\text{Ba}(\text{ClO}_4)_2+\text{Dy}_2\text{O}_3$  (0.25 mol%) mixture (Figs 1 and 4) indicate that the decomposition of the salt alone displays (i) initial gas evolution, (ii) an induction period, (iii) a short acceleratory stage and (iv) a long decay stage. The acceleratory and decay stages are distinguished from each other by a discontinuity at  $\alpha=0.5$ , corresponding to a phase change, i.e. semi-molten to solid. For the mixture, however, the reaction occurs through a short acceleratory stage and a long decay stage at lower temperatures, whereas the reverse phenomena are observed at higher temperatures. For both type of materials, the duration of the acceleratory period decreases, but the value of  $\alpha$  increases with increasing temperature and duration of heating, as shown in Table 3.

**Table 3** Values of fractional decomposition  $\alpha$  for  $\text{Ba}(\text{ClO}_4)_2$  and for  $\text{Ba}(\text{ClO}_4)_2+0.25$  mol%  $\text{Dy}_2\text{O}_3$  mixtures at different temperatures and after different time intervals

Time/min	Temperature/K				
	703	708	718	723	733
20	0.05	0.05	0.38	0.38	0.52
	0.31*	0.40*	0.48*	0.60*	0.66*
40	0.05	0.05	0.38	0.54	0.69
	0.52*	0.65*	0.68*	0.71*	0.85*

Values denoted by asterisks are for mixtures

The data are indicative of the fact that there is a 6-fold increase in the value of  $\alpha$  after 20 min of heating at lower temperature (703 K), which gradually decreases with increasing temperature.

## Kinetics of decomposition

Various theories based on the concept of nucleation and the growth of the nuclei, fitting topochemical aspects of solid-state decomposition have been discussed by many workers [8]. The kinetic equations employed are mainly based upon quantitative considerations of the nucleation and growth of the product phase. The structure of this phase, the types of strain generated in the solid, and the nature of the product interface play important roles in determining the kinetics of the reaction. During the decomposition, nuclei are generated either on the surface or in the interior of the solid, but decomposition proceeds via those growing along the lattice strain generating an array of product nuclei [9].

The data on the decompositions of the salt alone and its mixtures are analysed in light of different kinetic models with rate constants  $k_A$  and  $k_D$ , respectively, for the acceleratory and decay stages. According to Prout and Tompkins [10], the progress of decomposition along the lateral crevices may be termed a chain-branching model, conforming to the relationship.

$$\log \frac{\alpha}{1-\alpha} = k_{AD} t + C \quad (1)$$

where  $C$  is a constant term.

Data on both types of crystals are analysed through the use of Eq. (1), the range of applicability being  $0.07 < \alpha < 0.92$  (salt alone) or  $0.05 < \alpha < 0.96$  (mixture), respectively.

The normal lattice structures may also be susceptible to random nucleation within the entire crystal lattice, followed by two- or three-dimensional growth. These growing nuclei may overlap with each other, decreasing the reaction rate, according to the concept developed by Avrami and Erofeev [11, 12]:

$$[-\log(1-\alpha)]^{1/2} = k_{AD} t + C \quad (2)$$

The decomposition data on both types of materials fit well to Eq. (2), the ranges of applicability being  $0.07 < \alpha < 0.93$  (salt alone) and  $0.08 < \alpha < 0.90$  (mixture). The applicability of these equations to the present data suggests that, during the reaction, nucleation takes place in a chain-branching manner and two-dimensional growth of nuclei occurs.

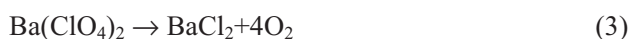
The rate constants of the acceleratory and decay stages, and the energy of activation ( $E \pm 5 \text{ kJ mol}^{-1}$ ) for the various processes (Table 4) indicate that in both types of samples  $k_A$  and  $k_D$  increase with increasing temperature, and at a given temperature  $k_A > k_D$ , irrespective of the kinetic equation employed; this may be a consequence of a cage effect. The interesting phenomenon is observed that the admixture enhances both rate constants notably, but without affecting the energy of activation.

**Table 4** Rate constants and activation energies for the decompositions of Ba(ClO<sub>4</sub>)<sub>2</sub> and of Ba(ClO<sub>4</sub>)<sub>2</sub>+0.25 mol% Dy<sub>2</sub>O<sub>3</sub> mixtures at different temperatures

	Rate constant·10 <sup>2</sup> / min <sup>-1</sup>	Temperature/K				
		703	708	718	723	733
Ba(ClO <sub>4</sub> ) <sub>2</sub>						
Prout–Tompkins	<i>k<sub>A</sub></i>	1.13	1.17	3.50	5.24	11.22
	<i>k<sub>D</sub></i>	0.15	0.21	0.43	0.54	1.17
Avrami–Erofeev	<i>k<sub>A</sub></i>	2.29	3.23	7.41	12.62	13.55
	<i>k<sub>D</sub></i>	0.20	0.68	1.28	1.73	3.16
Ba(ClO <sub>4</sub> ) <sub>2</sub> +0.25 mol% Dy <sub>2</sub> O <sub>3</sub>						
Prout–Tompkins	<i>k<sub>A</sub></i>	2.29	3.23	7.41	12.62	13.55
	<i>k<sub>D</sub></i>	0.50	0.68	1.28	1.73	3.16
Avrami–Erofeev	<i>k<sub>A</sub></i>	0.80	0.96	2.51	3.63	7.41
	<i>k<sub>D</sub></i>	0.20	0.39	0.53	0.72	1.34
Activation energy ( <i>E</i> ±5 kJ mol <sup>-1</sup> )						
		Prout–Tompkins		Avrami–Erofeev		
		<i>E<sub>A</sub></i>	<i>E<sub>D</sub></i>	<i>E<sub>A</sub></i>	<i>E<sub>D</sub></i>	
Ba(ClO <sub>4</sub> ) <sub>2</sub>		326.79	276.63	321.30	276.76	
Ba(ClO <sub>4</sub> ) <sub>2</sub> +0.25 mol% Dy <sub>2</sub> O <sub>3</sub>		323.15	267.89	318.20	267.54	

## Chemistry of decomposition

Barium perchlorate begins to decompose in vacuum at 778 K, and decomposition is complete after 9 h of heating:



a eutectic being formed between the solid product phase, BaCl<sub>2</sub>, and the host lattice.

The catalytic activity exerted by Ln<sub>2</sub>O<sub>3</sub> on the decomposition process may well be explained by their basicity, and in terms of an electron-transfer mechanism [13, 14].



The ClO<sub>3</sub><sup>-</sup> generated in step (i) may undergo further reaction to give rise to Cl<sup>-</sup> and O<sub>2</sub>. The Ln<sub>2</sub>O<sub>3</sub> are strongly basic in nature and donate electrons readily in step (i), resulting in a greater number of positive holes. Being *p*-type semiconductors the Ln<sub>2</sub>O<sub>3</sub> conduct better in an oxygen atmosphere [15] and enhance the decomposition

by capturing electrons from absorbed  $O^-$ . The catalytic effects of the admixtures depend upon the ease with which they can donate electrons, this being higher for more basic oxides. The sequence of basicity is  $La_2O_3 > Sm_2O_3 > Gd_2O_3 > Dy_2O_3$ , while the catalytic activity follows the  $La_2O_3 > Gd_2O_3 > Sm_2O_3 > Dy_2O_3$ . The difference in these sequences suggests that step (i) is not solely responsible for the reaction and step (ii) plausibly the rate-determining step, i.e. accepting an electron from  $O^-_{(ads)}$  is more important than its donation, supporting earlier data [15]. Gadolinium accepts electrons from  $O^-_{(ads)}$  to retain its trivalent state than does samarium, due to its stable half-filled 4f orbital, consequently favouring the reaction.

The admixture  $Dy_2O_3$  decreases the melting point and the decomposition temperature of  $Ba(ClO_4)_2$ , thereby increasing the reaction rate and the fractional decomposition  $\alpha$  without affecting the energy of activation.

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