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NON-ISOTHERMAL KINETIC STUDIES ON THE EFFECTS OF SEMI-CONDUCTIVE METAL OXIDES ON THE THERMAL DECOMPOSITION OF BARIUM PERCHLORATE TRIHYDRATE

FADHIL JASIM *, MAHMOOD M. BARBOOTI and KHALIL I. HUSSAIN
Department of Chemistry, College of Science, University of Baghdad, Baghdad (Iraq)

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ABSTRACT

The evaluation of kinetic parameters and mechanism of the thermal decomposition of barium perchlorate trihydrate (BP) from non-isothermal analytical measurements using TG, DTG, and DTA have been obtained in the presence of β-MnO_2 and Eu_2O_3. Both oxides catalyze the thermal decomposition of BP, and from the kinetic viewpoint they lower the activation energy by a factor of 2.5. Both of them remain chemically unchanged during the course of the decomposition of BP. A new mechanism has been proposed for the dehydration process to interpret the role of the oxide in it. Methods such as those of Freeman and Carroll and Coates and Redfern have been employed to estimate from TG curves, order of rection, activation energy, and pre-exponential factor for the thermal decomposition of BP, alone and in binary mixtures with each oxide. For the sake of checking, a modified computer program for the Coates and Redfern method has been introduced to compute the above mentioned parameters.

INTRODUCTION

The action of metal oxides on the thermal decomposition of oxo-salts has been the subject of several investigations [1–6]. The effects were most frequently catalytic and ascribed to the electrical semi-conductivity of the oxides at elevated temperatures [2,4,5]. The thermal decomposition of barium perchlorate trihydrate (BP) involves a multi-step dehydration, and the loss of four moles of oxygen per mole of BP to produce barium chloride [7]. Jacobs et al. [8] described a mechanism for the decomposition of BP into the chloride. The authors were able to explain the induction period of the reaction as well as the discontinuity as about 50% decomposition on the basis of their mechanism [8]. The reaction proceeds via the Avrami–Erofeev

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* To whom correspondence should be addressed.

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mechanism with an activation energy, E_a, and pre-exponential factor, log Z, of 80.9 kcal mole^{-1} and 20.7, respectively, for the reaction extent, $\alpha \leqslant 0.52$. Beyond this value of α, the E_a value is not more than 60.0 kcal mole^{-1} and log $Z = 13.1$ [7].

The purpose of the present work is to study the decomposition of BP in the presence of β-MnO_2 and Eu_2O_3 with the aid of TG, DTG, DTA, and XRD analysis.

EXPERIMENTAL

The apparatus and techniques used throughout this study were as described earlier [9] unless otherwise stated. The chemicals used were of analytical grade; $Ba(ClO_4)_2 \cdot 3\ H_2O$ from Hopkin and Williams, β-MnO_2 from Merck, and Eu_2O_3 from Fluka AG.

Procedure

The calculated amounts of the oxide and the BP were powdered and mixed in an agate mortar for 15 min. The 100 mg samples were placed in platinum crucibles of the type shown in Fig. 1, and heated at a rate of 10°C min^{-1} under static (air) atmosphere.

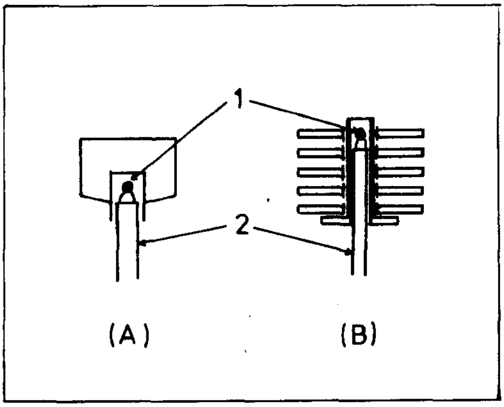

Fig. 1. The platinum crucibles used: (A) normal; (B) multiplate sample holder. 1, Thermocouple bead; and 2, porcelain rod.

RESULTS AND DISCUSSION

Decomposition of BP

The dehydration reaction, which involves the removal of three water molecules, starts above 40°C and finishes at 178°C. The water molecules seem to be bound in two different modes. One of the three molecules is lost below 110°C in a slow weight loss process. The particle size of BP affects both the shape and the position of the DTA peak. With relatively large crystals, the DTA peak occurs at 73°C, while for powdered samples it occurs at 63°C (Fig. 2). However, this effect almost vanishes when the multiplate sample holder [10] (Fig. 1) is used for heating, and the DTA peak appears at 65°C. The removal of the other two molecules of water is defined by two overlapping processes with DTA peak maxima at 144 and 178°C. The DTG curve also shows two peaks at 143 and 175°C. The reaction interval of each of these processes is narrow compared with that of the first molecule. Further, the multiplicity of the DTA peak which corresponds to the second stage of the dehydration refers therefore to the intermediate stages of this two-step reaction rather than a probable phase transition in the monohydrate as was claimed previously [7].

The partial and overall dehydration reaction, however, results in a de-

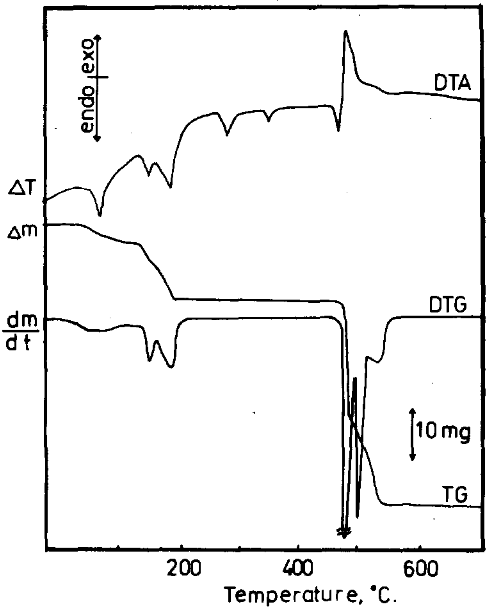

Fig. 2. Thermoanalytical curves of barium perchlorate trihydrate.

crease in the specific heat of the heated sample relative to the reference material (α-Al_2O_3). This is indicated by the rise of the baseline of the DTA curve. Such a decrease in the specific heat is due to the removal of water which has a high specific heat.

Pure anhydrous BP has shown thermal stability up to 460°C. In this temperature range two phase transitions, α to β and β to γ, occur [11]. These transitions are shown clearly on the DTA curve where two endotherms at 280 ± 0.4 and 350 ± 0.2°C (average of seven results ± the standard deviation) have been recorded. Throughout our investigations, the two endotherms related to these transitions are employed as fingerprints for the existence of the BP in the sample. Beyond 460°C BP undergoes decomposition at a rate fast enough to cause the sample to sputter out of the crucible. The thermograms show a discontinuity when the reaction extent reaches 0.52 ± 0.01. The results are identical to those reported earlier [7,8]. The DTA curve (Fig. 2) indicates that the process is characterized by a sharp endotherm at 472°C, sharp exotherm at 494°C, and a broad exotherm, corresponding to the slow decomposition, after the discontinuity. The assignment of these peaks was reported earlier [8].

When the sample was heated in the multiplate crucible, the discontinuity occurred at a higher value of α, i.e., 0.69 (Fig. 3). This compares favourably with the results obtained in ref. 7 where the discontinuity vanished under vacuum; thus the multiplate crucibles are to be recommended as an alternative for vacuum techniques.

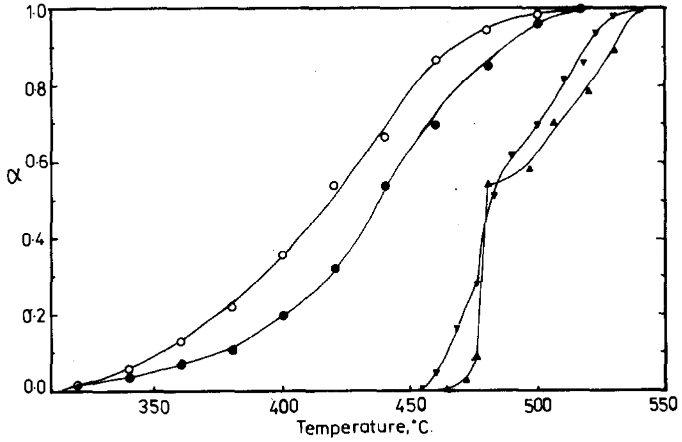

Fig. 3. Plots of the extent of decomposition, α, vs. temperature for the decomposition of BP with normal crucible, ▲; multiplate sample holder, ▽; in the presence of MnO_2, ●; and in the presence of Eu_2O_3, ○.

Effect of β-MnO$_2$

The TG, DTG, and DTA curves of intimate mixtures of β-MnO$_2$ and BP at molar ratios of 1 : 4, 1 : 2, and 1 : 1 are shown in Fig. 4. The dehydration of the salt occurs in two steps; two molecules are lost first and thereafter another one. This sequence differs from that observed in the dehydration of the individual salt (vide supra). A mechanism can be proposed for the role of the oxide in reversing the dehydration process as follows. Two of the water molecules must occupy adjacent sites and are linked similarly to the crystal of BP, the third one should occupy a remote site. The action of the oxide is to stabilize the monohydrate form of the crystal, rather than its dihydrate form, and therefore in the presence of the oxide two moles of water are expelled first.

The decomposition of BP is significantly altered by increasing the proportion of β-MnO$_2$. The fraction of the decomposed BP, α, of the 1 : 1 mole ratio is plotted against temperature (Fig. 3). The action of the oxide as a semi-conductive catalyst in this reaction is clear. The initial decomposition temperature was lowered to 310°C instead of 460°C for the individual BP. The catalytic decomposition is exothermic in all of its stages. At the 1 : 1 ratio, the reaction appears to be unique and is characterized by a broad

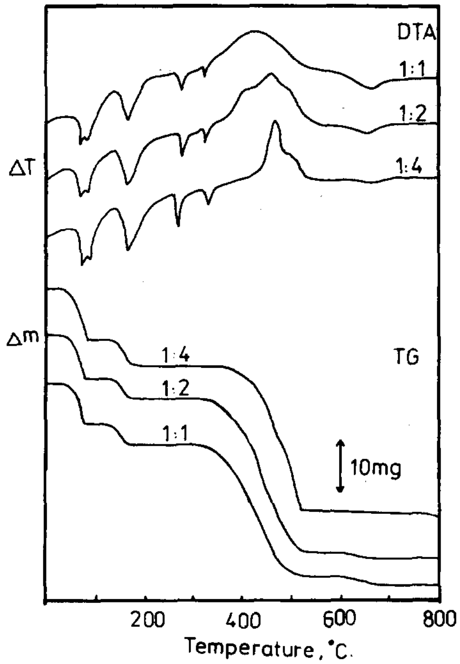

Fig. 4. TG and DTA curves of binary mixtures of MnO$_2$: BP at three molar ratios.

exotherm with a maximum at 431°C. The DTG peak maximum, however, occurs at a higher temperature (464°C) which means that the maximum value of the reaction rate takes place 30°C beyond the maximum rate of heat evolution. Consequently there exists an intermediate step more exothermic than the others throughout the reaction.

The TG and DTG curves of the mixtures indicate a slight weight loss between 610 and 680°C which increases with the increase of MnO_2 content of the mixture. This refers to the decomposition of β-MnO_2 into Mn_2O_3 [12]. Manganese(IV) oxide therefore acts entirely as a catalyst and remains unchanged during the course of the decomposition of BP. Shimokawaba et al. [4] suggested a mechanism for the action of semi-conductive metal oxides on the decomposition of alkali perchlorates. The ability of the oxide to abstract the oxygen radical from ClO_4^- can be regarded as the rate determining step. The less stable ClO_3^- so produced vanishes by decomposition into ClO_2^- and further into ClO^- [8].

TABLE 1

Assignment of the diffraction pattern of the 1 : 1 molar mixture of MnO_2 : BP cooled from 350°C

d-Spacing (Å) [a]	β-MnO_2	$BaClO_4)_2$· 3 H_2O [b]	Unknown
6.32		–	
5.67			–
4.34			–
3.64		–	
3.52			–
3.22			–
3.16			–
3.12	–		
2.79			–
2.39	–		
2.38			–
2.27			–
2.14	–		
2.10		–	
1.823		–	
1.819			–
1.752		–	
1.622	–		
1.581		–	
1.576		–	

[a] Above the line 2.000 the values are approximated to the nearest two figures.

[b] The salt is rehydrated on cooling and storage.

A sample cooled from 350°C gave the data shown in Table 1 when analyzed by X-ray diffraction. The diffraction patterns indicate matching BP, β-MnO_2, and another phase with bright lines at 3.16, 5.67, and 2.38 Å. This unidentified species may be a complex intermediate formed due to the catalytic decomposition of BP.

Effect of Eu_2O_3

Figure 5 shows the TG, DTG, and DTA curves for intimate admixtures of Eu_2O_3:BP at 1:4, 1:2 and 1:1 molar ratios. It is clear that the dehydration process is affected in the same manner as with manganese(IV) oxide. The DTA peaks corresponding to the phase transition of BP remain unchanged both in relative size and in position on the temperature axis. On the other hand, the thermograms undergo significant changes with increasing ratios of the oxide, as for the decomposition of pure BP. The initial decomposition temperature is lowered to 294°C compared with 460°C for the individual salt. A simple comparison of the behaviour of BP alone and as a mixture with Eu_2O_3 is seen in Fig. 3, where a curve of α vs. temperature for similar 1:1 Eu_2O_2:BP is drawn. The DTA curves of Fig. 5 reveal that similar steps

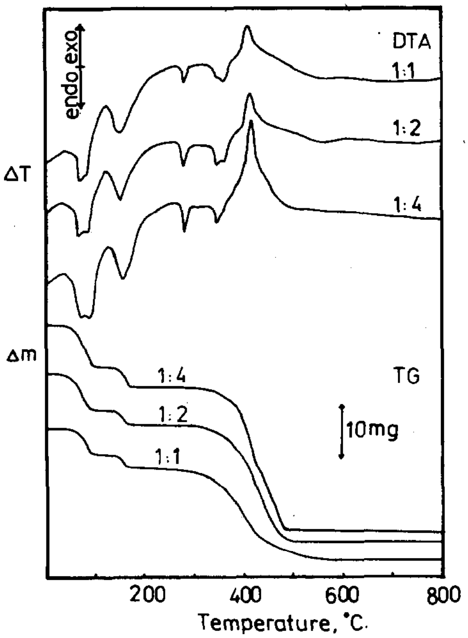

Fig. 5. TG and DTA curves of binary mixtures of Eu_2O_3:BP at three molar ratios.

(endo, exo, and broad exo) characterize the decomposition, although occurring earlier than with the individual salt. Accordingly, a similar mechanism for the dehydration and decomposition of BP may be presumed as in the case of β-MnO_2.

In order to check whether intermediate products have been formed during the course of the catalyzed reaction, the 1 : 1 molar mixture was cooled from 350°C and analyzed by XRD. The XRD pattern gave lines of $Ba(ClO_4)_2$, Eu_2O_3 and traces of $BaCl_2$.

Kinetic analysis of the results

The TG data presented in Fig. 3 have been used for the estimation of n, E_a, and log Z using the methods of Freeman and Carroll [14] and Coates and Redfern [13]. For the catalyzed decomposition, with β-MnO_2 or Eu_2O_3, the variant of the Freeman–Carroll equation

$$\frac{\Delta \log - \dfrac{d\alpha}{dt}}{\Delta \log(1-\alpha)} = n - \frac{E_a}{2.303R} \times \frac{\Delta(1/T)}{\Delta \log(1-\alpha)}$$

where $d\alpha/dt =$ the DTG signal, $R = 8.314$ J K^{-1} $mole^{-1}$ and $T =$ the absolute temperature, as reported by Segal and Fatu [15], is readily applicable. The results are listed in Table 2.

Zsako and Zsako [16] recently reported a computer program for the estimation of kinetic parameters, n, E_a, and log Z using the method of Coates and Redfern. The program, in FORTRAN language, has been used here after a slight modification to determine the kinetic parameters for the decomposition of BP with or without the oxides. The results are presented in Table 2.

Table 2 indicates that the E_a values for the decomposition of pure BP are comparable with those reported for its isothermal decomposition [7]. The thermal decomposition of BP appears to be a first order reaction, individually or in the presence of either oxide. According to Acheso and Jacobs [7], the reaction proceeds in accordance with the Avrami–Erofeev (A–E) mechanism. However, thermal decomposition reactions which follow the A–E mechanism are often found to follow first order kinetic equations and this is a contradiction [17]. Modification of the A–E equation [17] has been applied in our case and the data fitted well.

The catalytic action of β-MnO_2 and Eu_2O_3 is clear from the lowering of the activation energy of the decomposition of BP. The two oxides have comparable effects and both lower the activation energy by 2.5 orders of magnitude.

To explain the distinctive behaviour of β-MnO_2 towards the thermody-

TABLE 2

Kinetic parameters of the decomposition of BP, alone and in the presence of β-MnO_2 and Eu_2O_3, using the computer

Parameter	BP(C–R)		BP : Eu_2O_3		BP : MnO_2	
	$\alpha \leq 0.52$ [a]	$\alpha > 0.52$	F–C [a]	C–R	F–C [a]	C–R
n	1.00	1.03	1.06	1.17	0.52	1.03
E_a (kJ $mole^{-1}$)	225	84.0	103.7	103.0	110	86.0
log Z	22.5	8.0	10.5	10.4	11.0	8.6
Correl. Coef.	0.990	0.9705	0.9720	0.9980	0.966	0.9991

C–R = Coates–Redfern method; F–C = Freeman–Carroll method.

[a] Manual computation and plotting.

namics of the decomposition of BP (Fig. 4), an attempt has been made to determine the type of diffusion mechanism involved during the decomposition. Recently, Criado et al. [18] introduced a procedure whereby the diffusion mechanism of a thermal decomposition reaction can be determined on the basis of TG and DTG data. The procedure involves the evaluation of E_a/RT_m, where T_m is the temperature at which the rate of the reaction assumes the maximum value; they derived three expressions for the Ginstling–Brounstein, Jander, and the two-dimensional diffusion mechanisms to estimate the value of α at the point of maximum reaction rate for different values of E/RT_m. According to the valid diffusion mechanism, the predicted value of α_{max} at the practical E/RT_m value agrees with that obtained experimentally. Following on from this, the thermal decomposition of BP follows the Jander diffusion mechanism ($E/RT_m = 9.7$ and $\alpha_{max} = 0.54$ at 745 K). TG and DTG have been similarly employed to predict the diffusion mechanism for the decomposition of BP in the presence of either oxide. The reaction follows the Jander diffusion law in the case of Eu_2O_3 catalysis and the Ginstling–Brounstein law in the case of MnO_2 catalysis. The DTA curves have shown the discrepancy between the action of the two oxides. In the presence of β-MnO_2, the process has been found to be entirely exothermic; in the presence of Eu_2O_3 or BP alone, processes are characterized by endo, exo, and broad exothermic steps.

CONCLUSION

The non-isothermal kinetics can be correlated with those obtained from isothermal decomposition conditions, at least for the decomposition of $Ba(ClO_4)_2 \cdot 3\ H_2O$ into $BaCl_2$. The use of the multiplate sample holder for heating ensures partial vacuum conditions.

The thermal decomposition of BP is catalyzed by the metal oxides, for instance, β-MnO_2 and Eu_2O_3, when they are present in intimate mixtures with BP. The TG curves of the catalyzed decomposition can be studied kinetically. The action of the catalyst is to lower the activation energy of the decomposition reaction. The catalysis can extend further to change the mechanism of the reaction, for example, from the Jander diffusion into the Ginstling–Brounstein diffusion mechanism.

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