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Note

# THERMAL BEHAVIOUR OF BARIUM PERMANGANATE

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A simple method of preparation of complex oxides is the thermal decomposition of mixed metal complexes or oxometallates. Thus, Hardy [1] has reported that barium manganate, $BaMnO_4$, gives rise to barium manganite, $BaMnO_3$, on thermolysis at moderate temperatures. We report in this communication the thermal behaviour of barium permanganate, $Ba(MnO_4)_2$, following thermogravimetry and differential thermal analysis. The products of decomposition are characterized by X-ray powder diffraction patterns.

## EXPERIMENTAL

Barium permanganate, BP, is prepared using the known method [2]. The crystals gave $d_{hkl}$ values (Å) 5.78 m, 3.88w, 3.30s, 2.84m, 2.24m, 2.19m which agreed with the reported data [3]. The thermal decomposition studies were carried out both in air and flowing nitrogen on a Stanton thermobalance, Netzsch differential thermal analyzer, Stanton Redcroft STA 780 and Netzsch STA 429 thermal analyzers. Sample masses of approximately 10—20 mg were used and the rate of heating employed was 3—5° C $min^{-1}$, as large amounts and higher rates of heating caused splashing out of the sample from the container due to the high exothermicity of the reaction. The X-ray powder diffraction patterns were taken using Cu$K_\alpha$ radiation and a Debye—Scherrer camera of diameter 114.6 mm.

## RESULTS AND DISCUSSION

The thermal plots of BP in the temperature range 150—350° C and those in the region 400—750° C are given in Figs. 1 and 2, respectively. The plots in both air and nitrogen atmosphere are quite alike, suggesting that air does not influence the decomposition process of BP.

The TG curve suggests that BP is stable up to 180° C and apparently decomposes in two stages. The first stage of decomposition takes place in the temperature range 180—350° C accompanied by a weight loss of 12.5%, and the second stage occurs in the region 500—700° C with a loss of 4%. The decomposition is fast between 200 and 220° C and thereafter it is very sluggish. The DTA plot indicates that the reaction is exothermic with the peak maximum at 217° C.

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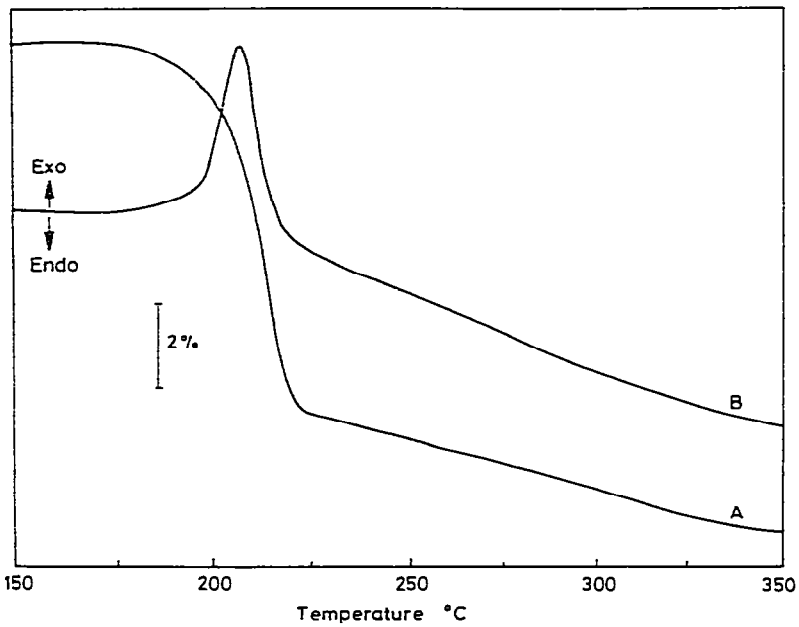


Fig 1 TG (A) and DTA (B) plots of $Ba(MnO_4)_2$ up to 400°C; rate of heating 3°C $min^{-1}$.

In a separate experiment a known amount of BP was heated slowly up to 400°C and the products obtained were examined by X-ray method. The $d_{hkl}$ values (Å) obtained were 3.42s, 2.88s, 2.24s, 1.75m, characteristic of

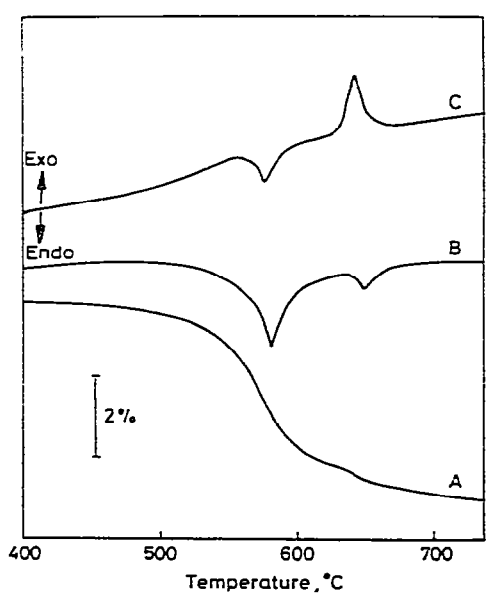


Fig. 2. TG (A), DTG (B) and DTA (C) plots of $Ba(MnO_4)_2$ between 400 and 750°C; rate of heating 5°C $min^{-1}$.

$BaMnO_3$ [4], and 3.15s, 2.44m, 2.18w, 1.69m, 1.59w, due to $MnO_2$ [5]. The observed weight loss was in agreement with the calculated weight loss of 12.8% for the formation of 1 mole each of $BaMnO_3$ and $MnO_2$ from 1 mole of $Ba(MnO_4)_2$.

The activation energy of the decomposition process is evaluated from the analysis of the TG curve using the method of Freeman and Carroll [6] and is found to be 27 kcal $mole^{-1}$.

Figure 2 shows the TG, DTG and DTA plots of the $BaMnO_3$ and $MnO_2$ mixture formed in the decomposition of BP. The DTG curve exhibits two peaks, at 575 and 630°C, suggesting two reactions occurring in this temperature range. The product of decomposition obtained at 750°C is found to have characteristic $d_{hkl}$ values (Å) 3.28s, 2.84s, 1.98m, 1.64w, due to BaO [6], and 5.10m, 3.14s, 2.79s, 2.52s, 2.11w, 1.56m, corresponding to $\gamma$-$Mn_2O_3$ [7]. It is known that $MnO_2$ decomposes above 500°C [8] and the endothermic peak observed at 575°C is assigned to the decomposition of $MnO_2$ to $Mn_2O_3$. Further, the exothermic peak observed at 630°C is probably due to the decomposition of $BaMnO_3$ to BaO and $Mn_2O_3$. The two processes overlap, resulting in an almost single-stage decomposition as observed in the TG curve. The total weight loss of 18% observed at 750°C is in agreement with the calculated weight loss (18.1%) for the formation of BaO and $Mn_2O_3$ from BP. It has been reported [9] that $BaMnO_3$ obtained by the thermolysis of $BaMnO_4$ loses oxygen above 900°C. However, the decomposition of $BaMnO_3$ at lower temperature in the present study may be due to the catalytic influence of $Mn_2O_3$ in its decomposition..

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