Thermochimica Acta, 32 (1979) 63–71

THERMAL BEHAVIOUR OF PARTIALLY REDUCED γ-MnO_2 IN ARGON ATMOSPHERE

A. AGOPSOWICZ, J. L. HITCHCOCK AND F. L. TYE
Berec Group Limited, Group Technical Centre, St. Ann's Road, London N15 3TJ (Gt. Britain)
(Received 31 August 1978)

ABSTRACT

Partially reduced samples of electrodeposited γ-MnO_2 having the general formula $(1 - n)\ MnO_2 \cdot nMnOOH$ with values of $n = 0.075$ to 0.825 were investigated by simultaneous TG, DTG and EGA in an argon atmosphere. Water evolution showing a peak rate at 260°C and increasing in total amount with increasing n was observed in agreement with previous work. However, subsequent oxygen evolution up to 900°C was found to occur at three clearly resolved stages, not two as previously reported for a similar range of compounds. By applying XRD after successive decompositions it was shown that the oxide Mn_5O_8 was formed during the water evolution stage according to the equation

$$(1 - n)\ MnO_2 \cdot n\ MnOOH \rightarrow \frac{n}{4} Mn_5O_8 + \frac{n}{2} H_2O + \left(\frac{4 - 5n}{4}\right) MnO_2$$

Residual MnO_2 decomposed into Mn_2O_3 with a peak rate at 540°C but the Mn_5O_8 was still present after the sample had reached 570°C. A separate oxygen evolution peak rate at 600°C was found to correspond to the decomposition of Mn_5O_8.

INTRODUCTION

A previous publication[1] reported the results of a thermogravimetric study in an oxygen atmosphere of a range of compounds having the general formula $(1 - n)\ MnO_2 \cdot nMnOOH$ with n values in the range 0.075 to 0.825. These oxides had been prepared by chemical reduction of an electrodeposited γ-MnO_2 with hydrazine. The thermal decomposition of the same range of compounds in an argon atmosphere has now been investigated by TG, DTG and EGA covering the temperature range ambient to 1000°C.

A number of previous authors[2–4] have reported three main decomposition stages in addition to the loss of physisorbed water:

(1) loss of water from hydroxyl groups;

(2) oxygen evolution resulting from the decomposition of the anhydrous oxide into Mn_2O_3;

(3) decomposition of Mn_2O_3 into Mn_3O_4 and oxygen.

In this work above 350°C oxygen evolution was observed to occur at three distinct stages instead of the two reported previously. The solid phases formed after successive decompositions were characterised by XRD. As a result of this study a new reaction scheme is proposed for the thermal decomposition of this range of compounds in inert atmospheres.

EXPERIMENTAL

Materials

The partially reduced oxides were prepared by the chemical reduction of a commercially available electrodeposited γ-manganese dioxide with hydrazine hydrate. The full details of the preparation of the samples and the determination of their formulae were described previously[1].

Apparatus and methods

Thermogravimetry was carried out using the Stanton Redcroft Thermobalance TG 750 with the DTG unit and a commercial electrolytic hygrometer (Salford

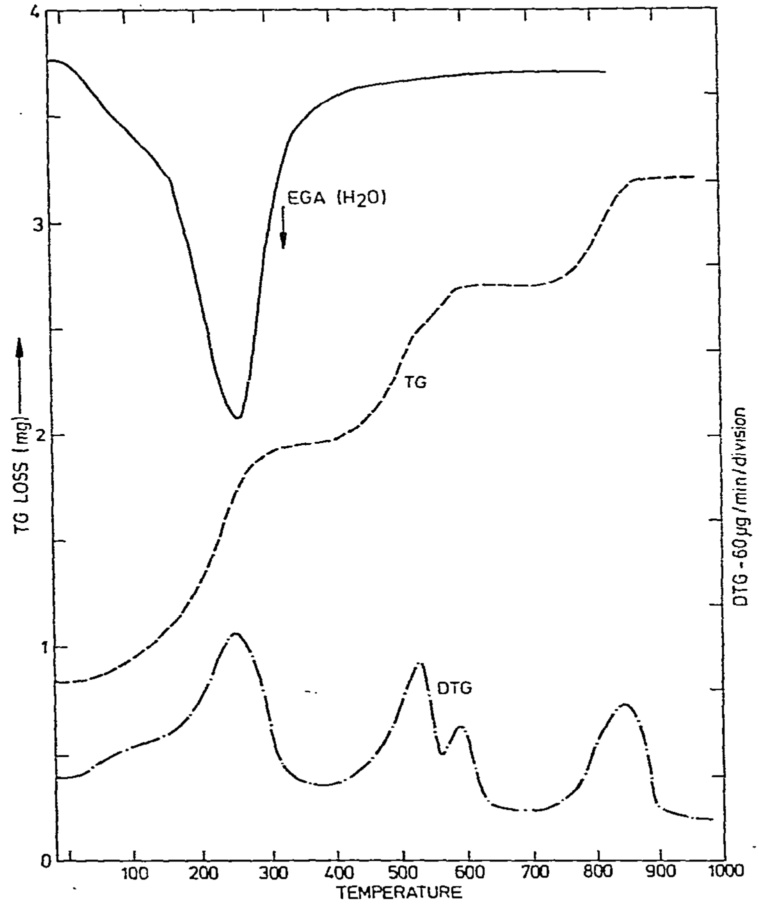

Fig. 1. TG, DTG and EGA curves in argon for the chemically reduced oxide, with degree of reduction $n = 0.480$.

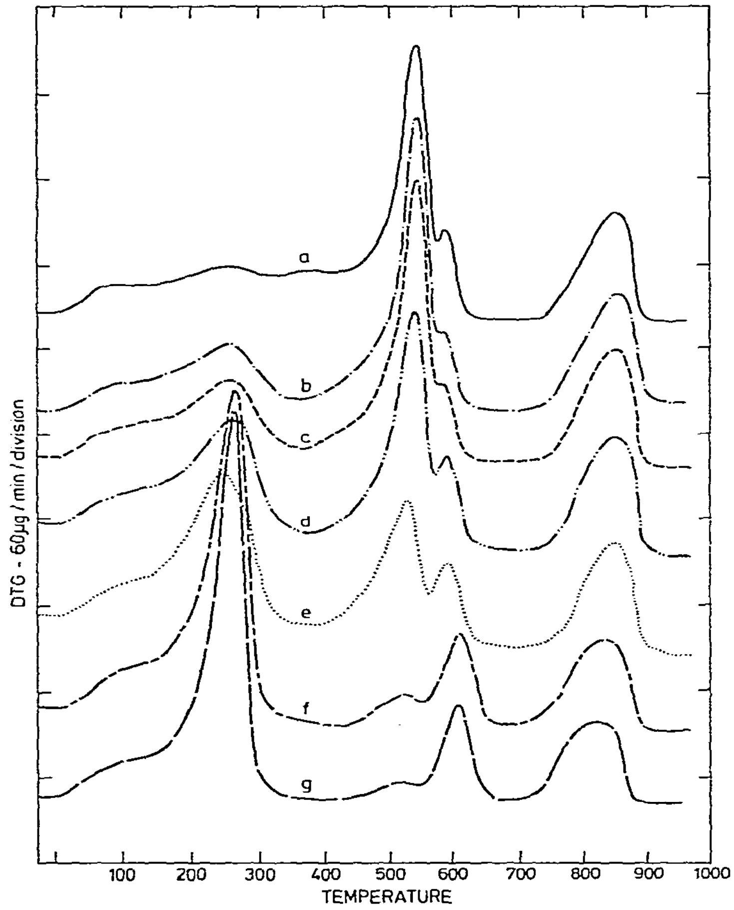

Fig. 2. DTG curves for γ-MnO_2 and its partially reduced oxides, with degree of reduction n equal to (a) 0.075, (b) 0.168, (c) 0.196, (d) 0.316, (e) 0.480, (f) 0.769, and (g) 0.825.

Electrical Instruments Ltd.) was coupled to the thermobalance to measure the evolved water. All the experimental conditions are essentially the same as in the previous work[1] except that the oxygen atmosphere was replaced with argon at a flow rate of 25 ml min^{-1}.

X-ray diffraction traces of the oxides were obtained with Philips diffractometer using the Cu K_α radiation.

RESULTS

Figure 1 is an example of the TG, DTG and EGA curves obtained. In contrast to the work in oxygen[1] the water loss gave rise to a single DTG and EGA peak. The DTG curves for all the samples are traced in Fig. 2. The quantities of oxygen evolved in each of the temperature regions 350–570 °C, 570–680 °C and 680–920 °C were determined from the TG curves. These quantities, calculated as the number of molecules of oxygen evolved per atom of manganese in the TG sample, are plotted as three sets of points in Fig. 4 and again in Fig. 5. XRD patterns given by the most

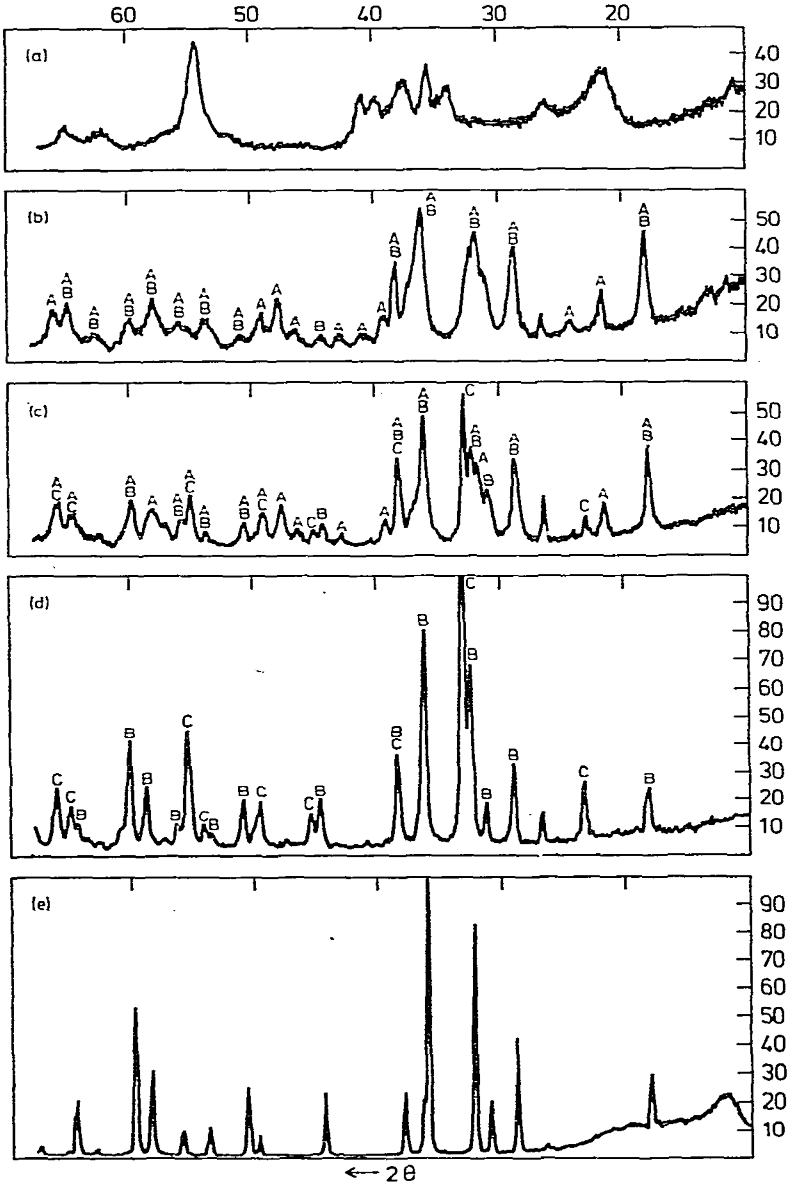

Fig. 3. X-Ray diffraction traces for the reduced oxide with degree of reduction $n = 0.825$, heated to various temperatures in argon: (a) untreated, (b) 350°C, (c) 570°C, (d) 680°C and (e) 920°C. A, B and C are X-ray diffraction lines, respectively, for Mn_5O_8, α-Mn_3O_4, and α-Mn_2O_3.

reduced sample, $n = 0.825$, and separate aliquots of the sample which had been heated in the thermobalance up to the temperatures shown and then cooled to ambient temperature while still in the argon atmosphere are shown in Fig. 3.

DISCUSSION

A gradual evolution of the DTG patterns was observed on passing stepwise from the least reduced to the most reduced samples as shown in Fig. 2. The novel feature of these patterns, particularly clear in the case of samples having intermediate

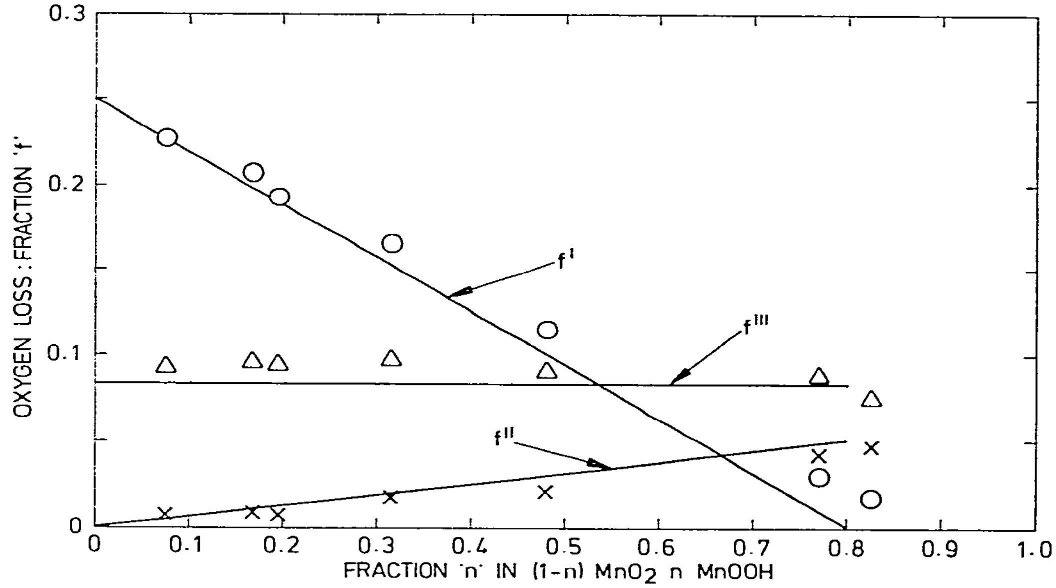

Fig. 4. Plots of $f' = (4 - 5n)/16, f'' = n/16$ and $f''' = 1/12$ vs. n, shown as continuous straight lines. The points are the experimentally determined weight losses expressed as molecules of oxygen per atom of Mn in the sample. Loss in the region 350–570 °C (○), 570–680 °C (×), and 680–920 °C (△).

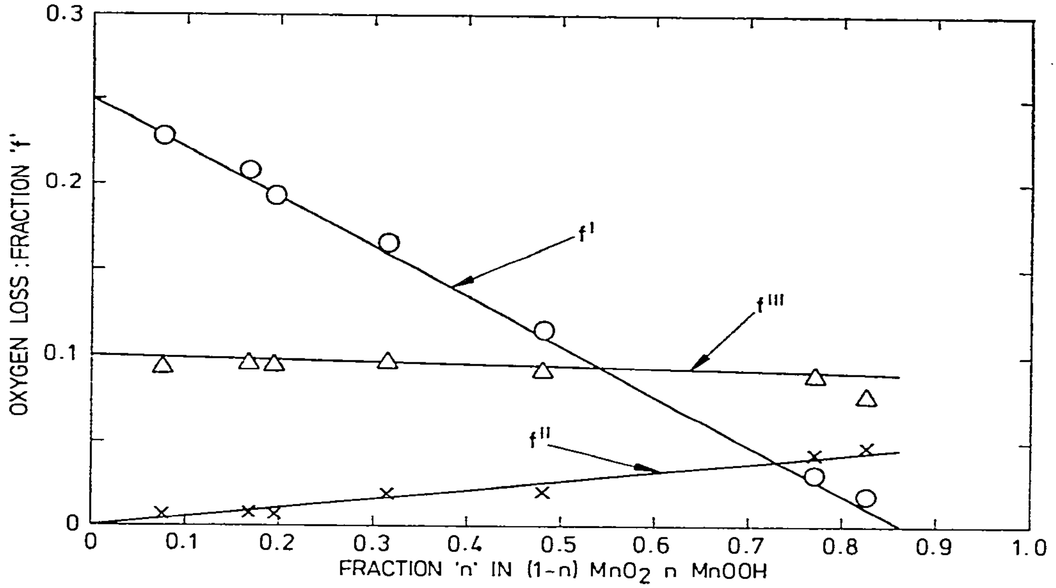

Fig. 5. Plots of $f' = (6 - 7n)/24, f'' = 5n/96$ and $f''' = (24 - 3n)/240$ vs. n, shown as continuous straight lines. The points are as in Fig. 4.

n values, is the evidence of four main decomposition steps. The EGA curves showed that water loss from the samples was complete by 350 °C. Subsequent weight losses must be due to oxygen evolution. The quantity of oxygen evolved in the region 350–570 °C was smaller the greater the n value (Fig. 4). However, in the temperature region 570–680 °C the quantity of oxygen evolved was greater, the greater the n value. Finally the oxygen loss in the region 680–920 °C was only slightly smaller, the greater the n value.

The third oxygen evolution stage could most readily be attributed to the well established decomposition of Mn_2O_3 into Mn_3O_4[2-6]. According to the classical reaction scheme the quantity of oxygen evolved at this stage should be independent of the n value. In the first oxygen evolution stage the quantity of oxygen evolved appeared to show a dependance on n that would be expected from the decomposition of MnO_2 into Mn_2O_3. The second evolution stage, wherein the quantity of oxygen evolved was surprisingly greater the greater the n value, was a newly discovered phenomenon. This stage was most marked with the sample having $n = 0.825$. Therefore it was with this sample that the solid phases before and after each decomposition were characterised by XRD. Figure 3(a) shows that the starting material was predominantly groutite although some manganite was present. Figure 3(b) shows that the XRD pattern of the solid remaining after heating to 350°C contains peaks at 2θ positions corresponding to all the d spacings listed by Oswald et al.[7] for the oxide Mn_5O_8 and these peaks account for most of the spectrum. The Mn_5O_8 pattern was still present after the sample had undergone a decomposition in the range 350–570°C (Fig. 3c). Additional weak lines appeared which can be ascribed to α-Mn_2O_3, particularly the line at $2\theta = 23.2°$ which is unique. The Mn_5O_8 was clearly destroyed during the decomposition in the range 570–680°C; note particularly the disappearance of the line at $2\theta = 21.6°$. Figure 3(d) shows that α-Mn_2O_3 and α-Mn_3O_4 were left. All that remained after heating to 920°C was α-Mn_3O_4 (Fig. 3e).

The formation of Mn_5O_8 has not previously been observed as a stage in the decomposition of partially reduced γ-MnO_2. Sato et al.[8] in the course of an investigation of γ-MnOOH noted the stability of a compound $MnO_{1.63}$ in the range 275–500°C in nitrogen but could not positively identify it as Mn_5O_8. This oxide can be prepared by controlled oxidation of γ-MnOOH at 400°C[9] or finely divided α-MnOOH below 300°C using oxygen[10]. It seems plausible to suggest therefore that oxides having $0 < n < 0.8$ could rearrange according to the following equation

$$(1 - n)\,MnO_2 \cdot n\,MnOOH \rightarrow \frac{n}{4}\,Mn_5O_8 + \frac{n}{2}\,H_2O + \left(\frac{4 - 5n}{4}\right) MnO_2 \qquad (1)$$

The quantity of Mn_5O_8 formed according to this equation, and available for subsequent decomposition, is proportional to n up to a maximum at $n = 0.8$.

Since Mn_5O_8 was not decomposed in the range 350–570°C yet oxygen was evolved and Mn_2O_3 was formed the process must have involved the MnO_2 formed in (1) as follows

$$\left(\frac{4 - 5n}{4}\right) MnO_2 \rightarrow \frac{4 - 5n}{8}\,Mn_2O_3 + \frac{4 - 5n}{16}\,O_2 \qquad (2)$$

The quantity of oxygen evolved at this stage is proportional to the MnO_2 formed in (1) and should also reach nil when $n \leqslant 0.8$. The decomposition of Mn_5O_8 which was observed in the region 570–680°C can be written either after Oswald et al.[7] as

$$4\,Mn_5O_8 \rightarrow 10\,Mn_2O_3 + O_2 \tag{3}$$

or after Newnham[11]

$$3\,Mn_5O_8 \rightarrow 5\,Mn_3O_4 + 2\,O_2 \tag{4}$$

The last decomposition stage, in the region 680–920°C, seems certain to be the decomposition of α-Mn_2O_3 to give α-Mn_3O_4 from the XRD evidence

$$6\,Mn_2O_3 \rightarrow 4\,Mn_3O_4 + O_2 \tag{5}$$

Further insight into the reactions taking place can be gained by considering the thermogravimetric data quantitatively. It will be useful to define the variables f', f'' and f''' as the number of molecules of oxygen evolved per atom of manganese in the sample in the temperature regions 350–570°C, 570–680°C and 680–920°C, respectively. On the basis of (2), $f' = (4 - 5n)/16$ so the plot of f' vs. n is a straight line having intercepts $f' = 0.25$ at $n = 0$ and $n = 0.8$ at $f' = 0$. Following Oswald's scheme (3) the Mn_5O_8 formed in (1) decomposes as follows

$$\frac{n}{4}\,Mn_5O_8 \rightarrow \frac{5n}{8}\,Mn_2O_3 + \frac{n}{16}\,O_2 \tag{3a}$$

hence $f'' = n/16$ and its plot vs. n is a straight line through the origin and the point $f'' = 0.05$ at $n = 0.8$. The total Mn_2O_3 formed in (2) and (3a) is $(4 - 5n)/8\ Mn_2O_3 + 5\,n/8\ Mn_2O_3 = \frac{1}{2}\ Mn_2O_3$. If its decomposition takes place according to (5) then $f''' = {}^1/_{12}$ and is independent of n.

The plots of f', f'' and f''' calculated according to the above formulae are shown as functions of n in Fig. 4 and do not match the experimental points accurately. It seemed as if in practice reaction (1) was not going to completion. This may be due to inhomogeneity of the sample or for kinetic reasons.

If the reaction proposed by Newnham[11] for γ-MnOOH

$$8\,MnOOH \rightarrow Mn_3O_4 + Mn_5O_8 + 4\,H_2O \tag{6}$$

is taking place in part it would explain also the observation of some α-Mn_3O_4 diffraction lines in Fig. 3(b). It was found that if the process taking place below 350°C was assumed to be a mixture of reactions (1) and (6) whereby two-thirds of the MnOOH fraction in the sample reacted by (1) and one-third by (6) all the calculated plots of f', f'' and f''' vs. n gave very good agreement with the corresponding experimental points, as shown in Fig. 5. According to (4) the plot of f'' vs. n would have met the abscissae at the same point as the f' plot. As this would have been in total disagreement with observation we favour reaction (3) to represent the decomposition of Mn_5O_8.

In deriving the calculated lines for f''' account was taken of the experimental fact that the final oxidation state of each sample corresponded very closely to $MnO_{1.30}$ and not $Mn_{1.33}$ as in Mn_3O_4. A final composition $MnO_{1.29}$ had been noted by

Brouillet et al.[4]. It may have been a sign of Mn_3O_4 beginning to decompose further to MnO as it has been shown to do on prolonged heating in vacuum[6].

Thus the following reaction scheme is in agreement with the XRD data and accounts quantitatively for the observed weight losses.

Below 350°C

$$ {}^2/_3 \times (1-n)\,MnO_2 \cdot n\,MnOOH \rightarrow {}^2/_3 \left\{ \frac{n}{4} Mn_5O_8 + \left(\frac{4-5n}{4}\right) MnO_2 + \frac{n}{2} H_2O \right\} $$

$$ {}^1/_3 \times (1-n)\,MnO_2 \cdot n\,MnOOH \rightarrow {}^1/_3 \left\{ \frac{n}{8} Mn_5O_8 + \frac{n}{8} Mn_3O_4 + \right. $$

$$ \left. + (1-n)\,MnO_2 + \frac{n}{2} H_2O \right\} $$

which adds up to

$$ (1-n)\,MnO_2 \cdot n\,MnOOH \rightarrow \frac{5n}{24} Mn_5O_8 + \frac{6-7n}{6} MnO_2 + \frac{n}{24} Mn_3O_4 + \frac{n}{2} H_2O \tag{7} $$

350–570°C

$$ \frac{6-7n}{6} MnO_2 \rightarrow \frac{6-7n}{12} Mn_2O_3 + \frac{6-7n}{24} O_2 \tag{8} $$

570–680°C

$$ \frac{5n}{24} Mn_5O_8 \rightarrow \frac{25n}{48} Mn_2O_3 + \frac{5n}{96} O_2 \tag{9} $$

680–920°C

$$ \frac{24-3n}{48} Mn_2O_3 \rightarrow \frac{24-3n}{80} Mn_3O_4 + \frac{24-3n}{240} MnO + \frac{24-3n}{240} O_2 \tag{10} $$

CONCLUSIONS

In the course of thermal decomposition in an inert atmosphere of compounds having the general formula $(1-n)\,MnO_2 \cdot n\,MnOOH$ some Mn_5O_8 is formed during the dehydroxylation stage. This is followed by three distinct decompositions with oxygen evolution, the second being the decomposition of Mn_5O_8.

ACKNOWLEDGEMENTS

The authors thank the Directors of the Berec Group Limited for permission to publish this paper and Mr. P. R. Skidmore for obtaining the X-ray diffraction data.

REFERENCES

1 J. L. Hitchcock and P. F. Pelter, *Proc. 4th ICTA, Budapest, 1974*, Vol. 1, p. 979.
2 J. P. Gabano, B. Morignat, E. Fialdes, B. Emery and J. F. Laurent, *Z. Phys. Chem.*, 46 (1965) 359.
3 L. Laragne and J. Brenet, *Bull. Soc. Chim. Fr.*, 9 (1968) 3499.
4 Ph. Brouillet, A. Grund, F. Jolas and R. Mellet, in D. H. Collins (Ed.), *Batteries 2*, Pergamon Press, 1965, p. 189.
5 D. M. Tinsley and J. H. Sharp, *J. Therm. Anal.*, 3 (1971) 43.
6 T. E. Moore, M. Ellis and P. W. Selwood, *J. Am. Chem. Soc.*, 72 (1950) 856.
7 H. R. Oswald, W. Feitknecht and M. J. Wampetich, *Nature (London)*, 207 (1965) 72.
8 M. Sato, K. Matsuki, M. Sugawara and T. Endo, *Nippon Kagaku Kaishi*, 9 (1973) 1655.
9 H. R. Oswald and M. J. Wampetich, *Helv. Chim. Acta*, 50 (1967) 2023.
10 R. Giovanoli and U. Leuenberger, *Helv. Chim. Acta*, 52 (1969) 2333.
11 C. E. Newnham, *J. Solid State Chem.*, 30 (1979).