Journal of Thermal Analysis, Vol. 10 (1976) 257—264

THE THERMAL DECOMPOSITION OF MANGANESE(II) SULPHITE TRIHYDRATE

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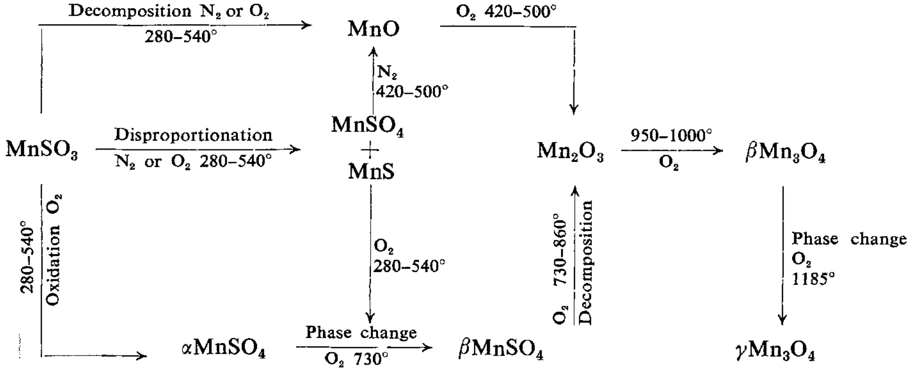
(Received March 3, 1976)

Thermal studies have shown that manganese(II) oxide and trimanganese tetroxide are the final decomposition products when manganese(II) sulphite trihydrate is heated in nitrogen and oxygen respectively. However, in each atmosphere, there are several decomposition routes involving the intermediate formation of manganese(II) sulphate and manganese(II) sulphide. The reactions can be summarized as follows:

$$MnSO_3 \cdot 3H_2O \xrightarrow[N_2 \text{ or } O_2]{60\text{–}120^\circ} MnSO_3 \cdot 2H_2O \xrightarrow[N_2 \text{ or } O_2]{120\text{–}160^\circ} MnSO_3 \cdot \tfrac{1}{2} H_2O \xrightarrow[N_2 \text{ or } O_2]{160\text{–}260^\circ} MnSO_3$$



Experimental

The decomposition reactions were studied using a Stanton Massflow vacuum and gas atmosphere thermobalance and a Netzsch 404 DTA apparatus. The X-ray powder diffraction of the starting materials and of the intermediate and final products was carried out using an iron target with a Siemens Kristalloflex 4 generator and a Siemens Diffractometer (Type F). The sulphur dioxide evolved during the decompositions using the Massflow thermobalance was determined by passing the evolved gases through bubblers and titrating with a standard solution of iodine using starch as indicator. Samples of manganese(II) sulphite trihydrate, of 99.9% purity with respect to $MnSO_3$, were prepared by the following methods.

Method 1 A concentrated solution of manganese(II) chloride was mixed with 45% w/v sodium hydrogen sulphite solution, the resulting precipitate washed in turn with water, alcohol and acetone, and the product dried in a vacuum desiccator.

Method 2 Sulphur dioxide was passed through a suspension of manganese(II) carbonate in water, the excess carbonate removed by filtration, and manganese(II) sulphite trihydrate allowed to crystallise from the filtrate in a vacuum desiccator.

Samples prepared by Method 2 were of much larger crystal size and tended to be more stable to oxidation at room temperature than samples prepared by Method 1.

Results obtained by thermogravimetry and differential thermal analysis

Several preparations of manganese(II) sulphite trihydrate were decomposed and Figs 1 and 2 are typical TG and DTA curves obtained in nitrogen, and Figs

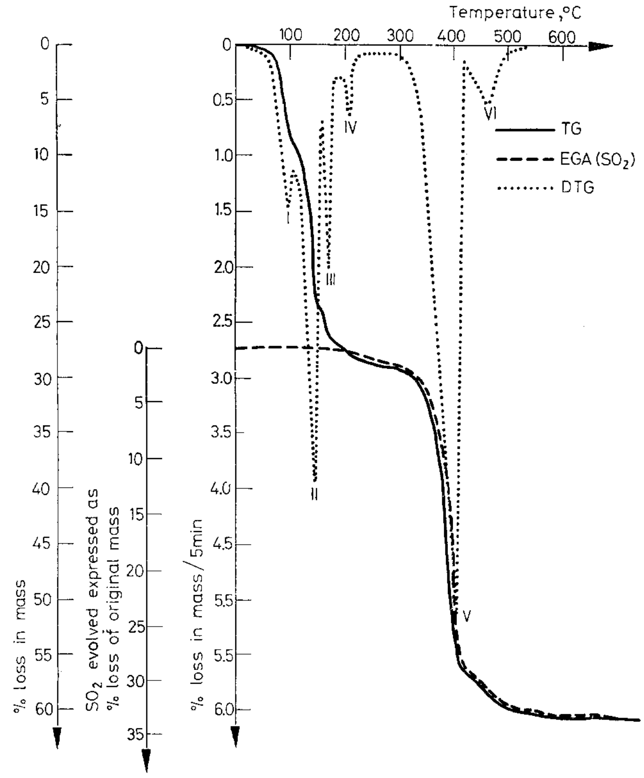


Fig. 1. TG, DTG and EGA of manganese(II) sulphite trihydrate in nitrogen

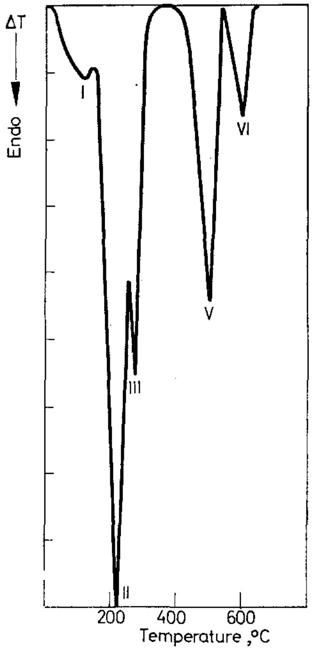


Fig. 2. DTA of manganese(II) sulphite trihydrate in nitrogen

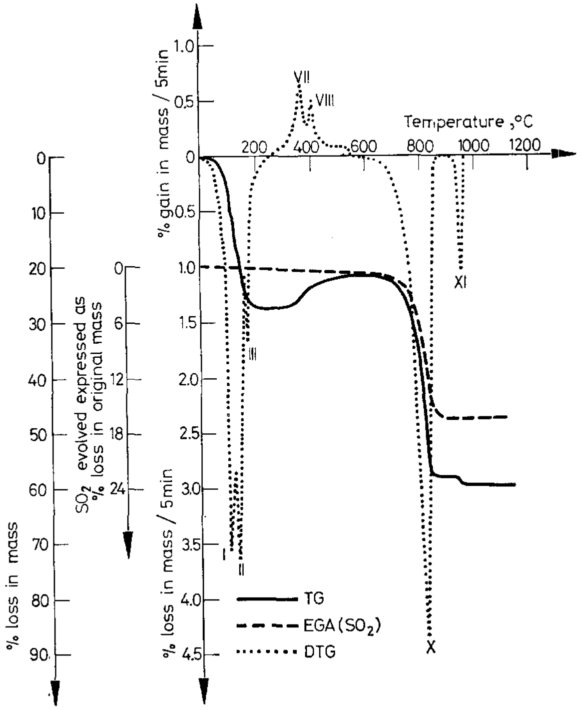


Fig. 3. TG, DTG and EGA of manganese(II) sulphite trihydrate in oxygen

3 and 4 the corresponding curves in oxygen. In both atmospheres the water of crystallisation was lost in three stages, peaks I, II and III, corresponding to the loss of 1, 1½ and ½ moles of water/mole of starting material.

During the final water loss a small amount of sulphur dioxide was lost from the sample, peak IV. Similar behaviour has been observed with other hydrated sulphites [1].

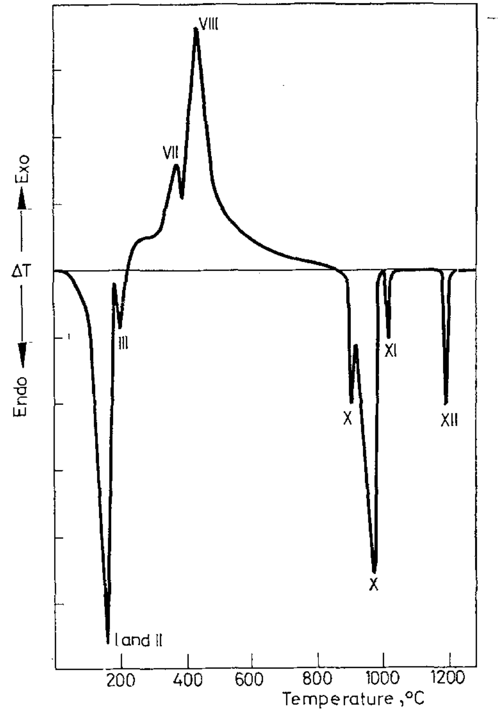


Fig. 4. DTA of manganese(II) sulphite trihydrate in oxygen

On further heating in nitrogen the manganese(II) sulphite underwent a two-stage decomposition, Figs 1 and 2, peaks V and VI, to give a loss corresponding to the formation of manganese(II) oxide and sulphur dioxide. Over the whole of this range the sulphur dioxide determined by titration agreed very closely with the loss in mass. There were no further mass losses on heating to higher temperatures.

When anhydrous manganese(II) sulphite was heated in oxygen there was a gain in mass due to its oxidation to manganese(II) sulphate, Figs 3 and 4, peaks VII and VIII. It was found that the relative sizes of these two exothermic peaks changed as the particle size of the sample was altered, and that there was a smaller percentage gain in mass with larger crystals of small surface area than with finely powdered samples because of the difficulty of penetration of oxygen through the sulphate formed on the surface. Complete oxidation of the sulphite to sulphate was never achieved and small amounts of sulphur dioxide were evolved during the oxidation. On further heating above 580° the following sequence of reactions was observed.

$$\begin{array}{llcll}
1 & \alpha MnSO_4 & \rightarrow & \beta MnSO_4 & \text{peak IX} \\
2 & 2MnSO_4 & \rightarrow & Mn_2O_3 + SO_2 + SO_3 & \text{peak X} \\
3 & 3Mn_2O_3 & \rightarrow & 2Mn_3O_4 + \tfrac{1}{2}O_2 & \text{peak XI} \\
4 & \beta Mn_3O_4 & \rightarrow & \gamma Mn_3O_4 & \text{peak XII}
\end{array}$$

Discussion

Although manganese(II) sulphite gave a quantitative yield of manganese(II) oxide and sulphur dioxide when heated in nitrogen, both the TG and DTA results indicated that the decomposition involved two stages. In addition the results obtained in oxygen showed that, after the samples had ceased increasing in mass, the amount of sulphur dioxide liberated above the decomposition temperature of the sulphite in nitrogen, was much greater than could be accounted for in terms of the decomposition of the manganese(II) sulphate formed on oxidation. X-ray powder diffraction of partially decomposed samples heated in nitrogen showed the presence of manganese(II) sulphate along with manganese(II) oxide and undecomposed manganese(II) sulphite. Every precaution was taken to avoid extraneous oxidation of the samples. Qualitative and quantitative chemical analysis of these residues also showed the presence of manganese(II) sulphide. X-ray powder diffraction failed to detect this phase probably due to its low concentration and poor crystallinity.

During the decomposition of manganese(II) sulphite in nitrogen there are two possible routes which involve the formation of manganese(II) sulphide and manganese(II) sulphate as intermediates. These phases may be formed either by a disproportionation reaction according to Eq. (6) [2] or by reaction of manganese(II) oxide with sulphur dioxide not yet expelled from the crucible, according to equation (7). At higher temperatures the sulphide and sulphate reacted together according to equation (8), so that the total decomposition corresponded to the quantitative formation of manganese(II) oxide and sulphur dioxide. The two stages in the decomposition in nitrogen are

$$\left.\begin{array}{llcl}
5 & MnSO_3 & \rightarrow & MnO + SO_2 \\
6 & 4MnSO_3 & \rightarrow & MnS + 3MnSO_4 \\
7 & 4MnO + 4SO_2 & \rightarrow & MnS + 3MnSO_4
\end{array}\right\}\text{Stage 1}$$

$$\begin{array}{llcll}
8 & MnS + 3MnSO_4 & \rightarrow & 4MnO + 4SO_2 & \text{Stage 2}
\end{array}$$

and these correspond to peaks V and VI as observed in both the TG and DTA experiments. Stages 1 and 2 overlap and the relative sizes of the peaks were dependent on the heating rate and particle size of the sample.

Two distinct stages were observed during the reaction of manganese(II) sulphite with oxygen to form manganese(II) sulphate. Peak VII was due to the oxidation of the sulphite at the surface of the original particles, and then, because of the disproportionation of the remaining sulphite to sulphide and sulphate, together with some decomposition to manganese(II) oxide and sulphur dioxide, both processes involving structural changes, further oxidation was possible giving rise to peak VIII. At the end of the oxidation reactions the intermediate residues were brown due to the presence of oxides of manganese. On further heating the decomposition temperature of the manganese(II) sulphate formed was slightly lower than that normally observed and the sulphur dioxide liberated above 650° was greater than that possible according to Eq. (2) even allowing for partial decomposition of the sulphur trioxide produced. These observations are due to the presence of manganese(II) oxide, which had been protected from oxidation, reacting with manganese(II) sulphate according to Eq. (9).

$$9 \qquad 2MnO + MnSO_4 \rightarrow Mn_3O_4 + SO_2$$

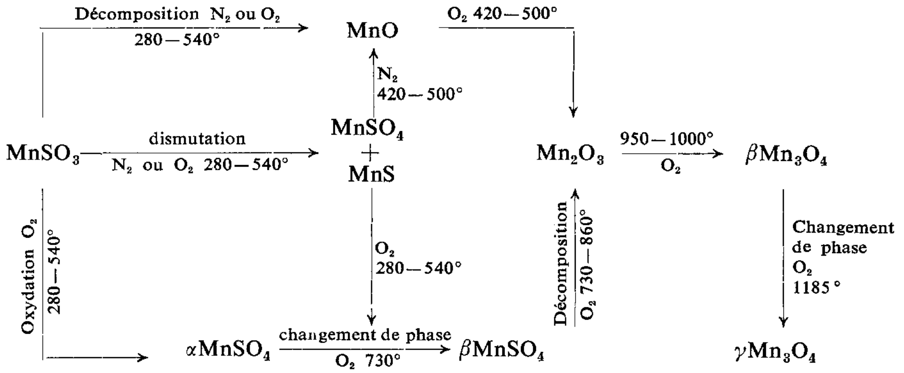
Substantiating evidence for the disproportionation of manganese(II) sulphite was obtained by heating a mixture of manganese(II) sulphide and manganese(II) sulphate in nitrogen [3] when endothermic reactions occurred between 500 and 700° according to equation (8). During these reactions there was a quantitative evolution of sulphur dioxide.

References

1. D. Dollimore and D. Nicholson, J. Inorg. Nucl. Chem., 25 (1963) 739.
2. M. A. Gorgen, Compt. Rend., 96 (1883) 341.
3. F. G. Buttler and S. R. Morgan, unpublished work.

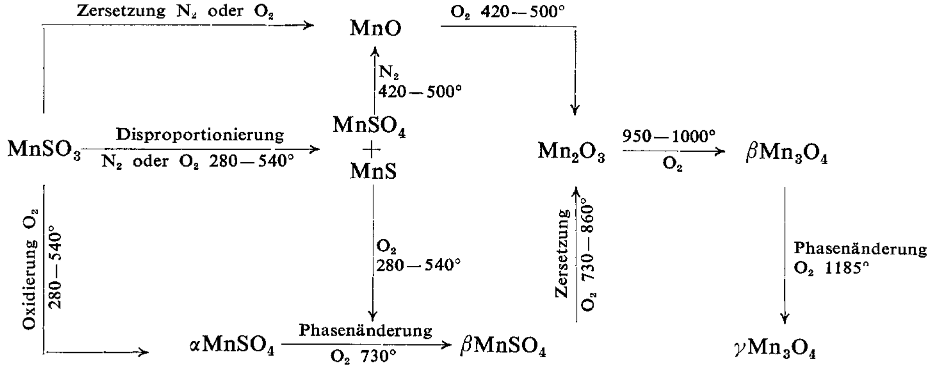
RÉSUMÉ — Les études thermiques montrent que l'oxyde de manganèse(II) et le tétroxyde de trimanganèse constituent les produits finaux de la décomposition du sulfite de manganèse(II) chauffé respectivement dans l'azote et dans l'oxygène. Cependant dans chacune de ces atmosphères, plusieurs chemins de décomposition peuvent être suivis. Ils font intervenir la formation intermédiaire de sulfate de manganèse(II) et de sulfure de manganèse(II). Les réactions peuvent être résumées comme suit:

$$MnSO_3\cdot 3H_2O \xrightarrow[N_2 \text{ ou } O_2]{60-120^\circ} MnSO_3\cdot 2H_2O \xrightarrow[N_2 \text{ ou } O_2]{120-160^\circ} MnSO_3\cdot \tfrac{1}{2}H_2O \xrightarrow[N_2 \text{ ou } O_2]{160-260^\circ} MnSO_3$$



ZUSAMMENFASSUNG — Thermische Untersuchungen haben gezeigt, daß Mangan(II)oxid und Trimangan-Tetroxid die Endprodukte der Zersetzung sind, wenn Mangan(II)sulfit Trihydrat in Stickstoff bzw. Sauerstoff erhitzt wird. In jeder der Atmosphären gibt es jedoch verschiedene Zersetzungswege, wobei vorübergehend Mangan(II)sulfat und Mangan(II)-sulfid gebildet werden. Die Reaktionen können, wie folgt, zusammengefaßt werden:

$$MnSO_3\cdot 3H_2O \xrightarrow[N_2 \text{ oder } O_2]{60-120^\circ} MnSO_3\cdot 2H_2O \xrightarrow[N_2 \text{ oder } O_2]{120-160^\circ} MnSO_3\cdot \tfrac{1}{2}H_2O \xrightarrow[N_2 \text{ oder } O_2]{160-260^\circ} MnSO_3$$



Резюме — Термическое изучение показало, что при нагревании тригидрат сульфита марганца в атмосфере азота и кислорода, в качестве конечных продуктов разложения образуютсая, соответственно, MnO и Mn_3O_4. Однако, в каждой атмосфере протекает несколько путей разложения, включая промежуточное образование сульфата- и сульфида марганца (II). Все реакции суммированы в виде следующей схемы:

$$MnSO_3 \cdot 3H_2O \xrightarrow[N_2 \text{ или } O_2]{60-120^\circ} MnSO_3 \cdot 2H_2O \xrightarrow[N_2 \text{ или } O_2]{120-160^\circ} MnSO_3 \cdot \tfrac{1}{2}H_2O \xrightarrow[N_2 \text{ или } O_2]{160-260^\circ} MnSO_3$$