

THERMAL DECOMPOSITION OF AQUEOUS MANGANESE NITRATE SOLUTIONS AND ANHYDROUS MANGANESE NITRATE. PART 1. MECHANISM

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ABSTRACT

The thermal decomposition of aqueous manganese nitrate solutions in air or nitrogen proceeds in three steps:

(i) partial evaporation of water to a concentrated solution containing equimolar amounts of water and $\text{Mn}(\text{NO}_3)_2$,

(ii) a first decomposition step in which the residual water evolves and part of the $\text{Mn}(\text{NO}_3)_2$ decomposes to MnO_2 , and

(iii) a second decomposition step in which the remaining $\text{Mn}(\text{NO}_3)_2$ decomposes to MnO_2 .

Decomposition of part of the $\text{Mn}(\text{NO}_3)_2$ in the first step is caused by the presence of water (vapour) which accelerates the decomposition of anhydrous $\text{Mn}(\text{NO}_3)_2$ and lowers the temperature at which this reaction starts. Without water [anhydrous $\text{Mn}(\text{NO}_3)_2$] only one decomposition step occurs.

Off-gas analysis with mass spectrometry, IR spectroscopy and chemiluminescence showed NO_2 to be the main gaseous product, NO being formed in much smaller amounts.

INTRODUCTION

Nowadays manganese dioxide is produced in increasing amounts by electrolysis of manganese sulphate solutions for use as depolariser in batteries [1]. This is a rather sophisticated and energy-intensive process. Therefore, an alternative process is being studied to obtain battery-grade manganese dioxide from manganese ore via a manganese nitrate solution. As part of this project the mechanism, kinetics and heat of reaction of the thermal decomposition of aqueous manganese nitrate solutions were studied. The results of an investigation into the mechanism are reported below.

LITERATURE

Hydrates

Ewing and Rasmussen [2] found the hydrates $\text{Mn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 2 \text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ to be stable in

the system $\text{Mn}(\text{NO}_3)_2\text{--H}_2\text{O}$, whereas in the system $\text{Mn}(\text{NO}_3)_2\text{--H}_2\text{O--HNO}_3$, besides these hydrates, the sesquihydrate and hemihydrate also occurred [3]. However, there is still some doubt about the existence of the latter two hydrates [4].

Structures

When comparing the crystal structures of the manganese nitrate hydrates with 6, 4, 2 and 1 molecule of H_2O , it follows that the manganese coordination changes from coordination by water molecules towards coordination by nitrate groups, and from six to eight coordination from $\text{Mn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ to $\text{Mn}(\text{NO}_3)_2 \cdot \text{Mn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ is orthorhombic and composed of $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ cations and NO_3^- anions, the cations and nitrate ions being held together by hydrogen bonds [5]. $\text{Mn}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ is monoclinic. In this case the Mn ions are surrounded by a distorted octahedron consisting of four oxygen atoms from H_2O molecules and two oxygen atoms from nitrate ions [6,7]. $\text{Mn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ is orthorhombic and contains two crystallographically different types of Mn atoms. One Mn atom is six-coordinated by oxygen atoms from four nitrate groups and two water molecules, whereas the other Mn atom is eight-coordinated by oxygen atoms from four nitrate groups which are bonded bidentately [8]. The structures of $\text{Mn}(\text{NO}_3)_2 \cdot 2 \text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2$ are not yet reported in the literature but the Mn ion in $\text{Mn}(\text{NO}_3)_2 \cdot 2 \text{H}_2\text{O}$ is probably six-coordinated by four oxygen atoms from monodentate nitrate groups and two oxygen atoms from water molecules. The Mn ions in anhydrous $\text{Mn}(\text{NO}_3)_2$ are believed to be eight-coordinated by four bidentate nitrate groups. This possibility is easily deduced from the structures of $\text{Mn}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ and especially $\text{Mn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$.

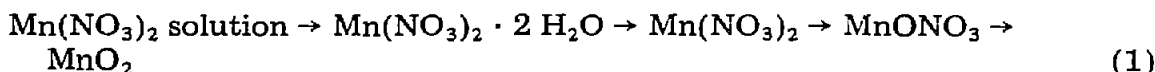
Water removal

In a desiccator with concentrated H_2SO_4 or P_2O_5 at 25°C a $\text{Mn}(\text{NO}_3)_2$ solution loses water to form $\text{Mn}(\text{NO}_3)_2 \cdot 2 \text{H}_2\text{O}$, according to Weigel et al. [4], whereas on prolonged drying over P_2O_5 pure $\text{Mn}(\text{NO}_3)_2$ was obtained by Ewing and Glick [3]. On heating, the solution loses water until $\text{Mn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ is formed, according to refs. 9 and 10 or until $\text{Mn}(\text{NO}_3)_2 \cdot 2 \text{H}_2\text{O}$, according to refs. 11–14 before nitrate decomposition starts. Under vacuum at 25°C , water evaporates to the composition $\text{Mn}(\text{NO}_3)_2 \cdot 2 \text{H}_2\text{O}$ which, when heated to 68°C , changes to $\text{Mn}(\text{NO}_3)_2$ anhydrate via the monohydrate [4]. Zdanovskii and Zhelnina [15] showed that when a $\text{Mn}(\text{NO}_3)_2$ solution with some HNO_3 is heated to 80°C only water vapour comes off in the beginning but later also HNO_3 . HNO_3 removal is almost complete when the $\text{H}_2\text{O}/\text{Mn}(\text{NO}_3)_2$ molar ratio has reached the value of 4.

In summary, the literature reports on the behaviour of manganese nitrate solutions are conflicting and it is not clear what hydrate will be obtained on heating.

Decomposition

Some questions concerning the nitrate decomposition are also still open. In almost all the literature, e.g. refs. 9–11 and 16, the decomposition took place in one step, but in refs. 12–14 two steps are reported. In the latter papers it was assumed that the $\text{Mn}(\text{NO}_3)_2 \cdot 2 \text{H}_2\text{O}$ formed first decomposes via $\text{Mn}(\text{NO}_3)_2$ anhydrate to an oxynitrate, MnONO_3 , which reacted further at slightly higher temperatures to MnO_2



Water vapour had a marked effect only on the second step, the activation energy being reduced from 122–139 kJ mole⁻¹ to 76–88 kJ mole⁻¹ [13]. Lumme and Raivio [11] found the decomposition to occur in one step with an activation energy of 99 ± 2 kJ mole⁻¹. On account of the above it was considered necessary to investigate the decomposition of aqueous manganese nitrate solutions in more detail in order to elucidate the cause of the differences noted here.

EXPERIMENTAL

Equipment

A Stanton-Redcroft and a Cahn RG(TGS-1) thermobalance were employed. Air, dried over a molecular sieve, flowed through the balance at a rate of 100 or 200 ml min⁻¹. The sample weight was normally in the range 1–5 mg but in one series of experiments it was varied from 0.5 to 23 mg. Isothermal as well as non-isothermal experiments were performed. Water vapour could be added to the gas flowing to the Cahn balance by saturating part of the gas flow. It must be noted that before the oven in the Cahn balance could be heated, it had to be switched to a standby position through which it was heated relatively fast to 55°C. Only after this preheat stage was heating at a selected and controlled rate possible. The off-gas of some thermobalance experiments was analysed for water vapour by a Keidel cell (Consolidated Electrodynamics Corporation, type 26-303). This instrument measures concentrations of water vapour between 1 and 1000 ppm in a gas flow of 100 ml min⁻¹. The gas to be analysed flows through a tube coated with P₂O₅, the water vapour adsorbs and is electrolysed forming H₂ and O₂. The current is a measure of the water vapour concentration.

Two separate experiments were performed in which the off-gas was analysed by a Varian MAT 311A high resolution mass spectrometer coupled to a computer for data collection. For each experiment the mass/charge ratio range of 10–100 was scanned very frequently. At the end of each experiment the computer calculated the intensities of the total ion current as well as the intensity of selected individual mass/charge ratios as a function of time (scans). It was also possible to generate the complete mass spectrum at a given time, which is necessary to obtain an impression of the relative im-

portance of the various masses. The off-gases of some experiments performed in the Stanton balance were also analysed by IR and chemiluminescence. With the chemiluminescence equipment it was possible to measure the relative importance of NO and NO₂. The method is based on the reaction of NO with O₃. These two gases react at low pressure (approximately 0.13 kPa) to form NO₂, of which a part (about 10%) is formed in an energetically activated state. When it reacts to stable NO₂ light is emitted; at constant O₃ concentration the light intensity is a measure of the NO concentration. The sum of the NO and NO₂ concentrations was measured by first converting all NO₂ thermally to NO. Thus, two experiments were necessary to determine NO as well as NO₂. Almost all final and some intermediate products of the thermobalance experiments were examined by X-ray diffraction using a Debye-Scherrer camera with FeK α radiation. The photographs were compared with photographs of so-called International Common Samples (ICS) [17], i.e. standard MnO₂ samples chemically or electrolytically prepared and made available mainly by battery manufacturers. Most of these samples show approximately the same diffraction pattern and have the gamma modification. The results were also compared with data on manganese oxides given in the ASTM or JCPDS indexes [18].

Material

An aqueous solution of reagent-grade manganese nitrate, obtained from J.T. Baker Chemicals Corp., was used in all experiments. The composition of the solution, 61.5 wt.% Mn(NO₃)₂, 2.4 wt.% HNO₃ and 36.1 wt.% H₂O, was calculated from analysis results for Mn²⁺ and NO₃⁻. The concentration of other components was below 0.01 wt.%. Theoretical weight losses up to certain compositions were calculated by assuming nitric acid to have been evaporated completely, in accordance with results obtained by Zdanovskii and Zhelnina [15].

RESULTS AND DISCUSSION

Thermogravimetry

When heating a sample very carefully and slowly, first water evaporates and the sample becomes increasingly viscous and under our conditions always attains the overall composition Mn(NO₃)₂ · H₂O. The liquid sample is then pink, very viscous and hygroscopic. Upon further heating small grey or black dots appear, the sample swells, bubbles escape and gradually the liquid is converted to a solid. This intermediate product is grey, also hygroscopic and much more voluminous than the initial liquid sample. Finally, during a second decomposition step the product turns black; the final product looks swollen and has large holes and pores. The rate of the first decomposition step normally becomes noticeable at 130–140°C and that of the second step at 180–190°C. A stable weight loss corresponding to anhydrous Mn(NO₃)₂ was never observed.

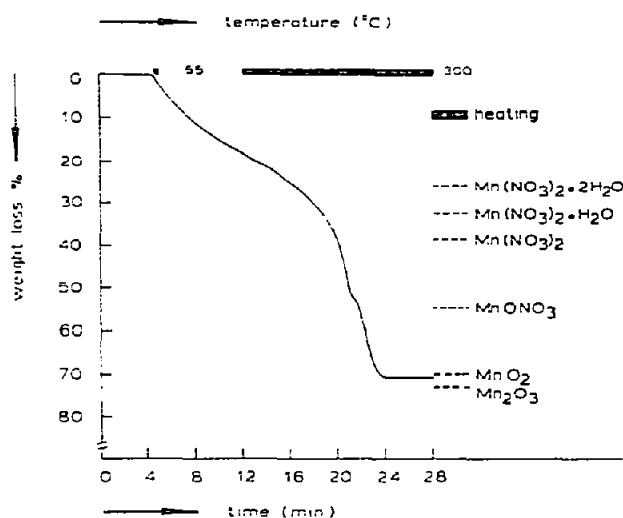


Fig. 1. Decomposition of manganese nitrate solutions; representative weight loss curve.

A representative weight loss curve measured with the Cahn balance is shown in Fig. 1, in which the weight loss as percentage of the initial weight is plotted against reaction time. First water evaporates to a composition of the solution between $\text{Mn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ which then decomposes in two steps. The term " $\text{Mn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ " does not mean that

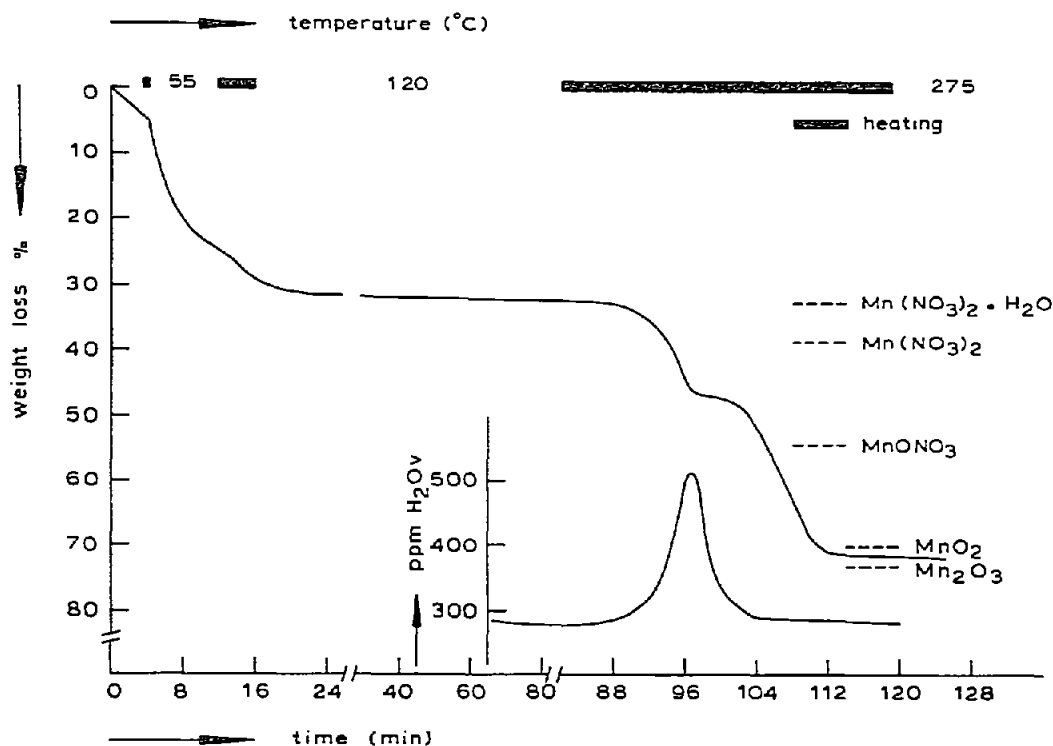


Fig. 2. Decomposition of manganese nitrate solution with off-gas analysis for water vapour.

crystals of this hydrate are actually present; it only indicates the overall composition, the ratio $\text{Mn}(\text{NO}_3)_2 : \text{H}_2\text{O}$ being 1 : 2. The weight loss of the first decomposition step is too large to result from residual water removal only and too small to correspond to the intermediate oxynitrate, MnONO_3 , assumed by Gallagher et al. [1,13,14]. The final weight loss corresponds to MnO_2 formation.

In Fig. 2 the result of heating a sample in steps is shown. The sample loses water at 120°C to give $\text{Mn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ and decomposes at 170°C to an intermediate product which again does not correspond to MnONO_3 , according to the weight loss. Finally MnO_2 is again obtained.

To determine during which decomposition step the residual water evolves from $\text{Mn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, the off-gas of the decomposition was analysed with a Keidel cell. After removal of most of the water to $\text{Mn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, the Keidel cell was connected and the sample heated to 275°C at a rate of 4°C min^{-1} . Figure 2 shows very clearly that all the residual water comes off during the first decomposition step. The amount of water vapour was calculated from the surface area of the water vapour peak after appropriate calibration of the Keidel cell. Approximately 1 mole of H_2O per mole of $\text{Mn}(\text{NO}_3)_2$ evaporated, which implies that the final product is virtually free of water.

To establish the effect of water vapour on the decomposition, it was added to the gas flow in known concentrations. At low temperatures the presence of water vapour results in sample weight increase, but when the temperature is raised the sample again loses weight. The resulting overall composition is a function of temperature and water vapour concentration. Furthermore, water vapour has a very marked influence on the reaction rate of the second decomposition step and on the temperature at which it starts. By heating a sample to 120°C the approximate composition $\text{Mn}(\text{NO}_3)_2 \cdot$

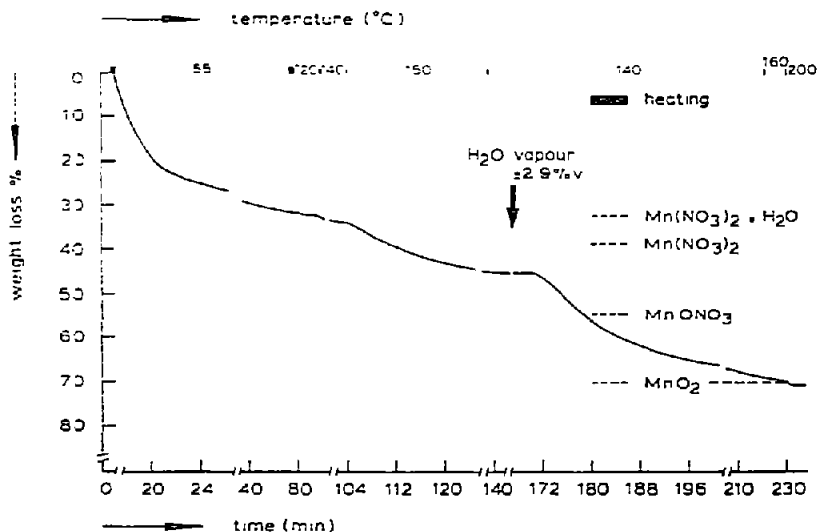


Fig. 3. Decomposition of manganese nitrate solution with addition of water vapour to the gas phase after the first decomposition step.

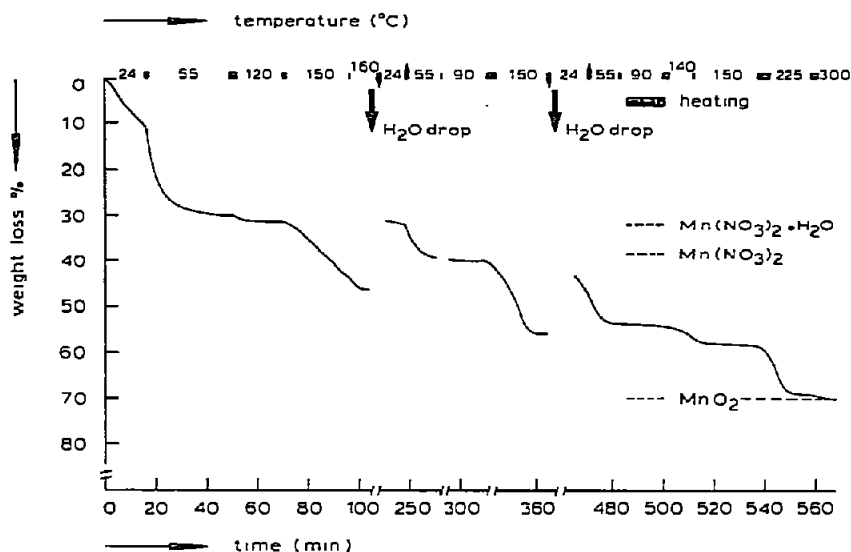


Fig. 4. Decomposition of a manganese nitrate solution with successive additions of water drops after the first decomposition step.

H_2O is obtained. This concentrated solution decomposes at 150°C to some unknown intermediate product in the usual manner. When it is cooled slightly to 140°C the weight of the intermediate product remains constant. However, after adding 2.9 vol.% water vapour to the gas phase the second decomposition step starts at this lower temperature and even goes to completion (Fig. 3). In another experiment a sample was cooled after the first decomposition at 150 – 160°C and then heated to 90°C after adding a drop of water. The weight did not return to its original value (Fig. 4). Heating to 140 – 150°C , at which temperature normally the first decomposition step occurs, again resulted in a decomposition step, which stopped at a lower weight level than the first time. Repeating this procedure of cooling, adding a drop of water, heating to 90°C and then to 140 – 150°C gave similar results (Fig. 4). Again the stable weight after the decomposition at 140 – 150°C was lower. Further heating resulted in decomposition to MnO_2 . Thus, each addition of water causes a new and partial first decomposition step.

It is concluded from the above experiments that water probably plays a vital role in the decomposition. This was confirmed by experiments with anhydrous $\text{Mn}(\text{NO}_3)_2$ prepared according to the method of Weigel et al. [4]. First most of the water of a $\text{Mn}(\text{NO}_3)_2$ solution was removed by passing air at 100 ml min^{-1} over it and heating the sample to 104°C . The air flow was then stopped and the sample brought under vacuum ($\approx 3 \text{ kPa}$). After pumping for 1.5 h, the pressure was raised to 0.1 MPa and the original air flow adjusted to 100 ml min^{-1} . The sample weight now corresponded very closely to $\text{Mn}(\text{NO}_3)_2$ (Fig. 5). The material was very hygroscopic and consisted of tiny dense particles. Heating revealed a strongly changed decomposition pattern: a first step was not observed and the weight loss during the second step was now much larger. Thus anhydrous $\text{Mn}(\text{NO}_3)_2$ decomposes in a single

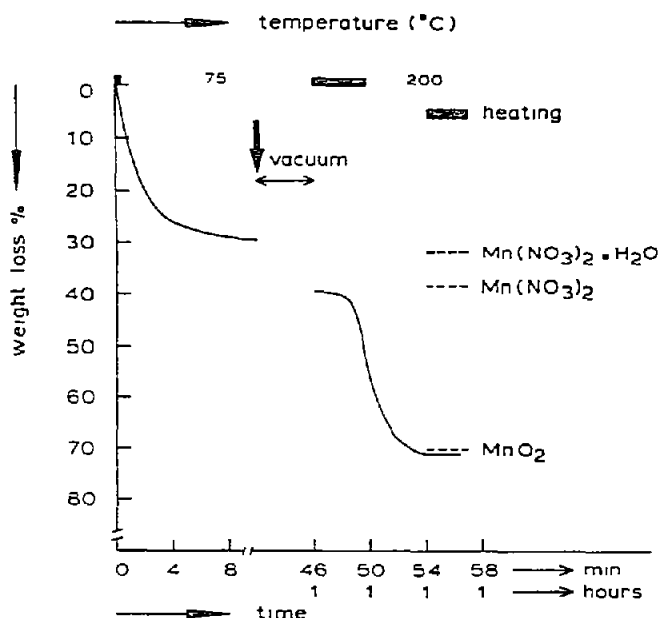


Fig. 5. Decomposition of a manganese nitrate solution with removal of water prior to the decomposition.

step, whereas the decomposition of $\text{Mn}(\text{NO}_3)_2$ with some water occurs in two steps.

Similar results were obtained when the experiments were performed in nitrogen.

Mass spectrometry (MS)

Mass spectrometry was used to confirm the above results and to determine which nitrogen oxides are formed. In the first experiment several mg of an aqueous $\text{Mn}(\text{NO}_3)_2$ solution were placed in a porcelain sample pan and heated to 300°C at a rate of $10^\circ\text{C min}^{-1}$ whilst passing helium over the sample. After removing most of the water, part of the off-gas was sucked into the mass spectrometer and analysed. The off-gas of the first decomposition step consisted almost entirely of water vapour, except for some NO ($m/e = 30$). This small amount of NO may have resulted from evolution of NO and/or NO_2 , because pure NO_2 gives its most important peak at $m/e = 30$ and not at $m/e = 46$ (intensity ratio 3 : 1). The picture changes in the second step. Now the largest peaks are NO ($m/e = 30$), and NO_2 ($m/e = 46$). Since in the mass spectrum the intensity ratio of the peak at $m/e = 30$ and $m/e = 46$ is close to 5, most of the peak at $m/e = 30$ comes from NO_2 , the remainder originates from NO. The peak at mass 44 could be attributed to only CO_2 by operating the mass spectrometer at very high resolution. The CO_2 had probably been dissolved in the solution. The ratio of the peaks at $m/e = 28$ (N_2) and 32 (O_2) is approximately unity instead of four, which means that some oxygen is also produced during the decomposition.

In a second experiment, about 1 mg $\text{Mn}(\text{NO}_3)_2$ solution was brought into

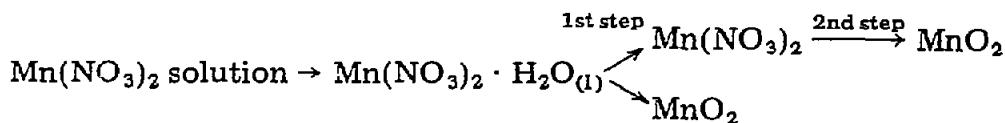
the high vacuum chamber of the mass spectrometer, and after 20 min heated to 300°C to remove most of the water. From thermobalance experiments under vacuum it is known that, by heating the solution, anhydrous $\text{Mn}(\text{NO}_3)_2$ is formed before the decomposition starts; thus only water is removed at first. This was verified by the mass spectra; all the peaks up to 150°C are caused by water which apparently evaporates very irregularly, perhaps in the form of escaping bubbles. During the single decomposition step that now occurred NO_2 and oxygen were formed. It is difficult to say whether NO was also evolved because the intensity ratio of the peak at $m/e = 30$ and $m/e = 46$ was approximately three, as is observed with pure NO_2 . However, since intensity fluctuations may occur it is not possible to exclude the presence of NO entirely. The peak at $m/e = 44$ was again caused by CO_2 .

IR Spectroscopy

The results obtained in the MS experiments were confirmed by IR spectroscopy measurements. Large sample weights (several hundred mg) and a smaller gas flow had to be employed to obtain a concentration of nitrogen oxides in the off-gas high enough to be measured. Only NO and NO_2 (N_2O_4) were found but no N_2O or other nitrogen oxides.

The MS and IR results fit in very well with the previous thermogravimetric data. They indicate that the first decomposition step is caused by water vapour and does not result in the oxynitrate, MnONO_3 , as an intermediate product. Reaction scheme (1) is thus unlikely. The intermediate product probably consists of a mixture of undecomposed $\text{Mn}(\text{NO}_3)_2$ and MnO_2 . This conclusion is based on the following measurements. First, experiments were carried out to establish the valence of Mn in the intermediate product. A product obtained by removing most of the water at 123°C and a subsequent first decomposition step at 177°C was rapidly cooled and then added to a solution of 2 N KOH with 5% tartaric acid. This acid is known to give a stable complex with Mn^{3+} ions. Polarographic analysis of the solution for Mn^{2+} , Mn^{3+} and Mn^{4+} showed Mn^{2+} and a trace of Mn^{4+} ; no Mn^{3+} was found. To strengthen this conclusion a sample prepared in an identical manner was dissolved in water and analysed for NO_3^- and Mn^{2+} . These two species were found in a molar ratio of 1.94, i.e. very close to the theoretical value for $\text{Mn}(\text{NO}_3)_2$ of 2.0. Furthermore, X-ray photographs taken of intermediate products made by decomposing the $\text{Mn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ solution at several temperatures showed lines of γ - and/or ρ - MnO_2 and occasionally very faint lines of γ - MnOOH . This result is further discussed when dealing with the X-ray data obtained.

In summary, everything points to an intermediate product consisting of a mixture of MnO_2 and $\text{Mn}(\text{NO}_3)_2$ and also to the conclusion that water vapour is responsible for the first decomposition step. The mechanism of the decomposition of the solution may be that during the first step water vapour evolves, forming bubbles in the viscous liquid. In the bubbles the water vapour concentration is fairly high, causing some $\text{Mn}(\text{NO}_3)_2$ to decompose at the liquid-gas interface. The reaction stops when all water vapour has escaped. In the second step the rest of $\text{Mn}(\text{NO}_3)_2$ decomposes to MnO_2 .



In view of the structure of $\text{Mn(NO}_3)_2 \cdot \text{H}_2\text{O}$ crystals in which two differently surrounded Mn ions occur, it is not unlikely that even in the liquid many Mn ions will be surrounded as in a crystal. Chemically speaking one could postulate a mechanism in which the Mn ions surrounded by 2 H_2O and 4 NO_3^- groups start to decompose to MnO_2 , whereas the Mn ions surrounded by four bidentate NO_3^- groups will decompose at higher temperatures. If so, one would expect a constant weight loss after the first decomposition step, because MnO_2 and $\text{Mn(NO}_3)_2$ are produced in equimolar quantities (overall MnONO_3). However, the measured weight loss is much too small for this. Therefore, a decomposition caused by water vapour which is no longer bound to Mn ions and which attacks the $\text{Mn(NO}_3)_2$ is more realistic. This water vapour adsorbs and probably causes a change in the manganese coordination and the configuration of the nitrate groups in the anhydrous $\text{Mn(NO}_3)_2$, resulting in an acceleration of the decomposition and a lowering of the temperature at which the decomposition starts. This mechanism also accounts for the observation that relatively large variations in weight loss up to the second decomposition step occur, which is caused by the unpredictable physical process of swelling and break-out of the water vapour bubbles.

The above mechanism might result in a dependence of the weight loss of the first decomposition step on sample weight. Therefore, a series of non-isothermal experiments was performed in the Stanton balance, the sample size being varied between 0.5 and 23 mg, using different heating rates and 100 ml min^{-1} air. The weight loss up to the second decomposition step increases with sample weight irrespective of the heating rate used ($3\text{--}20^\circ\text{C min}^{-1}$) (Fig. 6). This is a logical consequence of the proposed mechanism because it

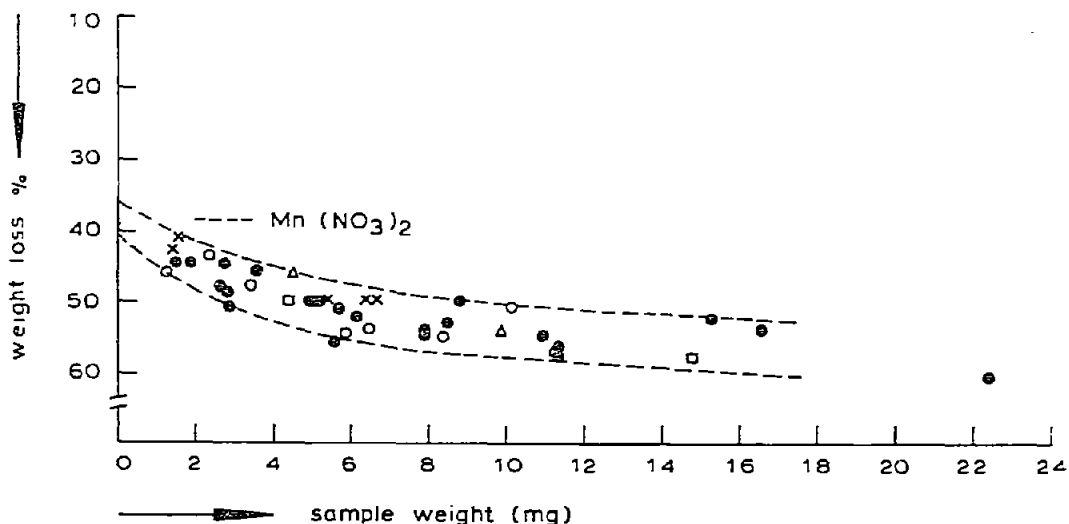


Fig. 6. Weight loss up to the second decomposition step as a function of sample weight. Heating rate: \odot , 3°C min^{-1} ; \times , 5°C min^{-1} ; \circ , $10^\circ\text{C min}^{-1}$; \triangle , $15^\circ\text{C min}^{-1}$; \square , $20^\circ\text{C min}^{-1}$.

is more difficult and takes more time for the water vapour to emerge from a larger "particle", so it has more time to attack $\text{Mn}(\text{NO}_3)_2$ and to promote its decomposition. This also explains why certain authors (e.g. refs. 9–11 and 16) found the decomposition to occur in one step. They all used very large sample weights ($\gg 100$ mg) which causes the second step to disappear. Moreover, sample weights of approximately 15 mg 45.4 wt.% $\text{Mn}(\text{NO}_3)_2$ solution, such as were used by Gallagher et al. [12], corresponds to approximately 11 mg of the 61.5 wt.% $\text{Mn}(\text{NO}_3)_2$ solution used in this study. Figure 6 shows that for samples of this size the observed weight loss is 52–58% of the initial weight. This result comes very close to the theoretical weight loss of 54.3% for the intermediate oxide MnONO_2 postulated by Gallagher et al. [12]. If the band of weight losses for the different sample sizes of Fig. 6 is extrapolated to zero sample weight, it is found that the effect of the escaping water vapour on the $\text{Mn}(\text{NO}_3)_2$ decomposition disappears with infinitely small samples. The weight loss then is 36–41%, which agrees well with the theoretical weight loss to anhydrous $\text{Mn}(\text{NO}_3)_2$ of 38.5%. Other experiments in which the gas flow was varied between 40 and 150 ml min^{-1} showed no dependence on the gas flow of the weight loss up to the second step. This means that the weight loss of the first decomposition step is governed by conditions inside the "particle".

Chemiluminescence

Chemiluminescence measurements were made to quantify the relative amount of NO and NO_2 in the off-gases of the two decomposition steps and

TABLE 1
Chemiluminescence results

Sample wt. (mg)	Component analysed	Decomp. step	Yield per mg sample (%)	Ratio NO or NO + NO_2 1st/2nd step	Weight loss ratio of NO + NO_2 1st/2nd step	NO in total NO_x (%)
1.70	NO	1	2.1	0.68		9.1
	NO	2	3.1			4.0
0.99	NO + NO_2	1	23	0.80	0.12	
	NO + NO_2	2	77			
4.82	NO	1	1.5	1.5		3.8
	NO	2	1.0			1.6
3.48	NO + NO_2	1	39	0.64	0.59	
	NO + NO_2	2	61			
3.99	NO	1	1.2	2.0		3.1
	NO	2	0.6			1.0
3.60	NO + NO_2	1	39	0.64	0.63	
	NO + NO_2	2	61			
8.72	NO	1	1.9	3.8		2.6
	NO	2	0.5			1.9
10.60	NO + NO_2	1	74	2.8	2.3	
	NO + NO_2	2	26			

to determine whether a significant difference occurred in the ratio of NO and NO₂ depending on the decomposition step. Pairs of experiments were performed to measure the amount of NO and NO + NO₂ using sample weights around 1, 4 and 10 mg. The samples were decomposed in the Stanton thermobalance under 100 ml min⁻¹ N₂ and part of the off-gas was led into the chemiluminescence equipment. For each sample weight the amounts of NO and NO + NO₂ were separately established for both decomposition steps and calculated per mg initial sample weight. The total yield of NO_x (NO + NO₂) per mg initial weight was taken as 100% (Table 1, column 4). In column 5 the ratio is given of the yield of NO or (NO + NO₂) in the first step to the yield in the second step. In column 6 the same ratio is given, now calculated from the weight losses observed. The assumption was made that the weight loss of the second step is exclusively caused by NO_x evolution and the weight loss of the first step by loss of residual H₂O and some NO_x. The weight of the latter quantity of NO_x was calculated by subtracting the weight of the water from the weight loss observed. The nitrogen oxides which evolve during both decomposition steps apparently consist almost entirely of NO₂, the amount of NO being only 1–3%. With increasing sample weight more and more NO_x evolves during the first step; the ratio of total NO_x from the first step to total NO_x from the second step increases from 0.30 to 2.8 for sample weights from 1 to 10 mg. These ratios agree well with those obtained from the measured weight losses (column 6). The NO fraction of the NO_x produced in the first decomposition step seems to be a little higher than the percentage in the second step (column 7); however, the absolute differences are very small. So, most of the decomposition of both steps probably occurs according to the same mechanism. The results obtained provide additional proof that the proposed mechanism of a first decomposition step results in a mixture of MnO₂ and anhydrous Mn(NO₃)₂.

X-Ray results

In the ASTM and JCPDS indexes two types of γ -MnO₂ are distinguished, viz. MnO₂ produced electrolytically or chemically. The electrolytically prepared MnO₂ (EMD) differs from the chemically prepared MnO₂ (CMD) by showing a diffraction pattern containing less lines. The diffraction pattern of final and intermediate products obtained by decomposing Mn(NO₃)₂ solutions closely resembled each other. They corresponded well with EMD (ASTM index 14-644), except for a line at $d = 143$ pm which should be present in CMD but not in EMD (see Table 2). When comparing the diffraction lines of our products with the five strongest lines of ρ -MnO₂ (ASTM index 12-714), it is found that this extra line also coincides. The lines of low intensity which should be present in ρ -MnO₂ are missing except one. The diffraction patterns were also compared with the patterns of several International Common Samples (ICS Nos. 1-5 and 8-10). The patterns of the products corresponded almost exactly to that of the chemically prepared IC samples (Nos. 5 and 8), and differed from the electrolytically prepared IC samples 1–4, 9 and 10 in that some lines had slightly shifted (Table 2). Photographs of IC samples as well as decomposition products showed a

TABLE 2

Diffraction patterns

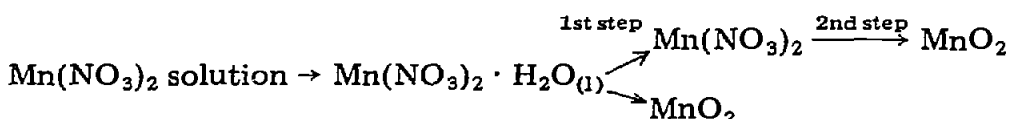
γ -MnO ₂ CMD ASTM 14-644 d(pm)	γ -MnO ₂ EMD ASTM 14-644 d(pm)	ρ -MnO ₂ ^a ASTM 12-714 d(pm)	ICS ^c CMD d(pm)	ICS ^d EMD d(pm)	Products d(pm)	
396	142.2	396	400	370 ^e	400 ^e	390—400 ^e
260	136.2	242	243	241	240	242
242	130.6	212	212	212	211	212
232	125.0	163.7	165	163	163	163
212	121.1	106.6	143	143	138.5	143
205	116.9		107 ^b	106	106	106
163.7	110.4					
160.5	106.6					
148.6						

^a Five strongest lines; ^b weak line; ^c ICS Nos. 5, 8; ^d ICS Nos. 1-4, 9, 10; ^e diffuse.

broad diffuse line around $d = 370$ – 400 pm. It is concluded that our product closely resembles both γ - and ρ -MnO₂. In all products MnO₂ was the only or main component. Sometimes, however, faint lines of γ -MnOOH (ASTM 18-805) were found and the strongest line of Mn₂O₃ (ASTM 10-69) was present on the photographs of very rapidly heated samples ($\geq 100^\circ\text{C min}^{-1}$). X-Ray photographs of the intermediate product showed identical though slightly more diffuse patterns.

CONCLUSIONS

The thermal decomposition of aqueous manganese nitrate solutions can be represented by the simplified scheme



On heating, most water evaporates until a composition of the solution of about 1 mole H₂O per mole Mn(NO₃)₂ is reached. This amount of H₂O cannot be removed at 0.1 MPa without causing some Mn(NO₃)₂ to decompose; at 130–140°C the residual H₂O begins to evolve, causing some MnO₂ formation. This decomposition stops when all water vapour has been removed. On further heating, the remaining Mn(NO₃)₂ decomposes to MnO₂. Thus, the first decomposition step is solely caused by water, which accelerates the Mn(NO₃)₂ decomposition and also lowers the temperature at which the decomposition starts. Water probably changes the bonding of the nitrate groups to manganese in anhydrous Mn(NO₃)₂, facilitating the decomposition. If the water is not present there is no first decomposition step; anhydrous Mn(NO₃)₂ then decomposes in a single step. The main gaseous

product of both decomposition steps is NO_2 , only a few percent NO being formed.

The $\text{Mn}(\text{NO}_3)_2$ probably decomposes in both steps according to the same mechanism; significant differences in NO_x off-gas composition between both decomposition steps were not observed.

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