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THE THERMAL DECOMPOSITION OF AQUEOUS MANGANESE (II) NITRATE SOLUTION

P. K. GALLAGHER, F. SCHREY AND B. PRESCOTT
Bell Telephone Laboratories, Inc. Murray Hill, New Jersey 07974 (U. S. A.)

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ABSTRACT

The thermal decomposition of commercially available aqueous solutions of manganese(II) nitrate was investigated using the conventional thermal analytical techniques of thermogravimetry (TG), differential thermal analysis (DTA), and evolved gas analysis (EGA). Infrared spectra and X-ray diffraction patterns were used to help characterize intermediate species.

TG and DTA experiments were performed in both wet and dry oxygen and nitrogen. The solution rapidly looses water around 100°C until it approaches a glassy type material near $Mn(NO_3)_2 \cdot 2H_2O$. Between 200–300°C the material loses, in close succession, its remaining water, a molecule of NO_2 to form $MnONO_3$, and finally another NO_2 to form MnO_2. The intermediate manganese(III) oxynitrate cannot be isolated. Wet atmospheres reduce the temperature separations between these reactions. Between 500–550°C the MnO_2 loses oxygen to form Mn_2O_3 and finally at 800–1000°C Mn_3O_4 is formed.

INTRODUCTION

Semiconducting manganese(IV) oxide is used to form an electrode on the dielectric layer of tantalum(V) oxide in the production of tantalum capacitors. Briefly, this layer or coating is obtained by dipping the porous, partially sintered, and anodized tantalum mass into a solution of manganese(II) nitrate. The tantalum is withdrawn and heated to decompose the adhering solution to manganese(IV) oxide. The anodizing, dipping, and firing processes are repeated as often as necessary to assure a satisfactory product. An understanding of the nature and rate of the thermal conversion of aqueous manganese(II) nitrate to manganese(IV) oxide, therefore, has considerable relevance to the technology associated with the production of tantalum capacitors. It is the purpose of this work to establish the stoichiometry and general nature of the thermal decomposition so that meaningful kinetic studies can be performed.

Ewing *et al.*[1–3], have extensively studied the system $Mn(NO_3)_2$–HNO_3–H_2O. In the binary portion, excluding nitric acid, they observed as stable solid phases a hexahydrate, tetrahydrate, dihydrate, and monohydrate species. Hegedus *et al.*[4], investigated the thermal decomposition of the tetrahydrate. They observed a plateau in their weight loss curve at a composition between the mono- and di-hydrate species. This material then decomposed directly to a composition near manganese(IV) oxide in the region of 70–200°C without any evidence of intermediate species. Between 480 and 560°C this material lost oxygen to yield manganese(III) oxide. They found that the presence of small amounts of organic or other reducing matter gave rise to a direct decomposition to manganese(III) oxide without the formation of manganese(IV) oxide. Therefore, the specific objectives of this work are to determine if any crystalline hydrate phases appear upon rapid evaporation of a standard commercially available manganese(II) nitrate solution, if there are any intermediate oxynitrate compounds formed, and finally if these solutions contain sufficient impurities to interfere with the normal scheme of the decomposition.

EXPERIMENTAL PROCEDURE AND RESULTS

Materials

Aqueous manganese(II) nitrate was obtained from Fisher Chemical Company, reagent grade lot No. 713972 (density = 1.55) and the Lehigh Valley Chemical Company, capacitor grade (density = 1.65). Small portions of these solutions were evaporated then heated at 250°C overnight. Table I presents the results of emission spectrographic analysis of the residues. There was no difference in behavior of the two solutions other than water content and consequently only data for the Fisher material is reported upon further.

TABLE I

EMISSION SPECTROGRAPHIC ANALYSIS OF RESIDUES FROM COMMERCIALLY AVAILABLE AQUEOUS SOLUTIONS OF $Mn(NO_3)_2$

Wt%	*Fisher Chemical Company*	*Lehigh Valley Chemical Company*
10^{-1} *x*	Mg	Mg
10^{-3} *x*	Cu	
10^{-4} *x*	Ca, Fe, K[a]	Ca, Cu, Fe[a]

[a] Low part of range.

Thermogravimetry (TG)

A Perkin–Elmer thermobalance was employed. The output was digitized and placed on paper tape as described elsewhere[5,6]. Runs were performed at 10°C/min in a flow of approximately 25 ml/min of oxygen or nitrogen. Both dry and wet atmospheres were used. The input gas was passed through either columns of Drierite and silica gel or a bubbler which saturated the gas with water vapor at room temperature. Approximately 0.01 ml of sample was placed on the small platinum sample pan. Temperature calibration was accomplished by the use of magnetic standards as described elsewhere[5]. Fig. 1 shows the computer output for a typical TG experiment. Fig. 1a is the conventional percent weight loss plot while 1b is a plot of the derivative (DTG) or rate of weight loss for the same run. Table II summarizes the TG results. In order to account for the variable small amounts of vaporization which took place during sample handling and prior to the beginning of weighing, all TG results were

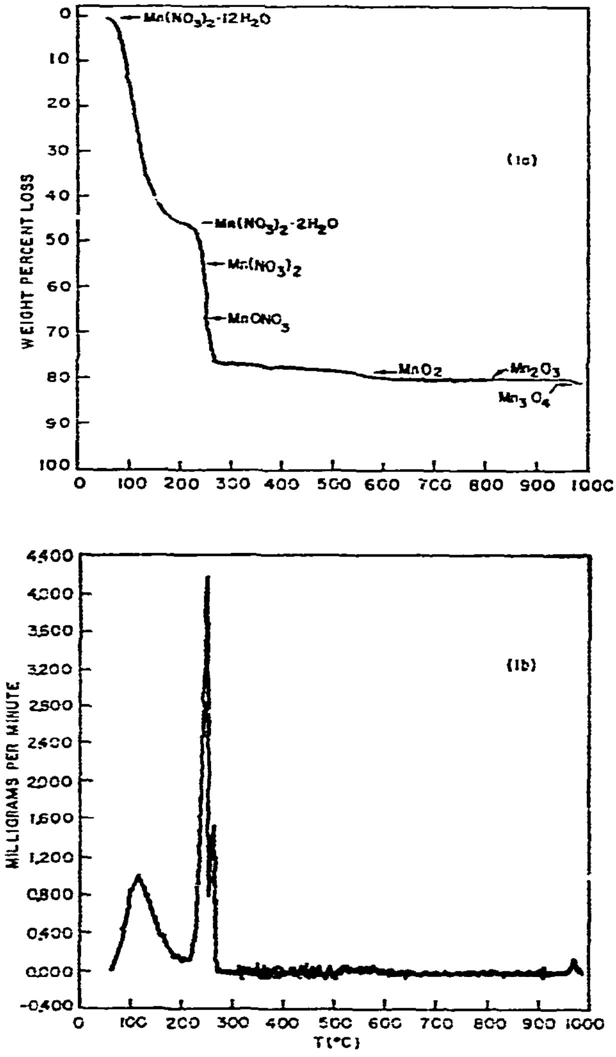

Fig. 1. Weight loss of aqueous $Mn(NO_3)_2$ (18.0 mg) in moist oxygen as a function of temperature; a, percent weight loss; b, rate of weight loss.

normalized to the composition of Mn_2O_3 at 750°C. The weight loss data given in Table II for the first two steps corresponds to that occurring at the minima in the DTG curves. The weight loss associated with manganese(IV) oxide was picked somewhat arbitrarily at 500°C because of the slow weight loss between 300 and 500°C. The last two reduction steps give the actual region of the reaction.

TABLE II

RESULTS OF THE TG EXPERIMENTS USING AQUEOUS $Mn(NO_3)_2$

Product	*% Wt. loss calc.*	*Oxygen*				*Nitrogen*			
		Dry		*Wet*		*Dry*		*Wet*	
		°C	*% Wt. loss*	*°C*	*% Wt. loss*	*°C*	*% Wt. loss*	*°C*	*% Wt. loss*
$Mn(NO_3)_2 \cdot 2H_2O$	45.5	25–200	46.9	25–205	45.8	25–178	47.2	25–187	46.6
$MnONO_3$	66.3	200–270	72.9	205–257	69.4	178–261	71.7	187–252	68.7
MnO_2	78.0	270–500	77.6	257–500	78.2	261–500	78.2	252–500	78.7
Mn_2O_3	80.0	500–760	80.0	500–650	80.0	500–550	80.0	500–650	80.0
Mn_3O_4	80.7	950–1000	80.7	950–1000	80.9	780–850	80.8	830–875	80.8

Differential thermal analysis (DTA)

A DuPont Model 900 thermalyser was used in conjunction with its differential scanning calorimeter cell. Aluminum sample pans were employed and the gas flowed over the sample at the approximate rate of 300 ml/min. The heating rate was 10 °C/min and chromel–alumel thermocouples were used. One drop of sample was placed in the sample pan and an empty sample pan served as the reference. Fig. 2 gives the results in dry oxygen and oxygen that has been saturated with water vapor at room temperature. The curves in nitrogen were very similar and exhibited comparable shifts in temperature with water vapor.

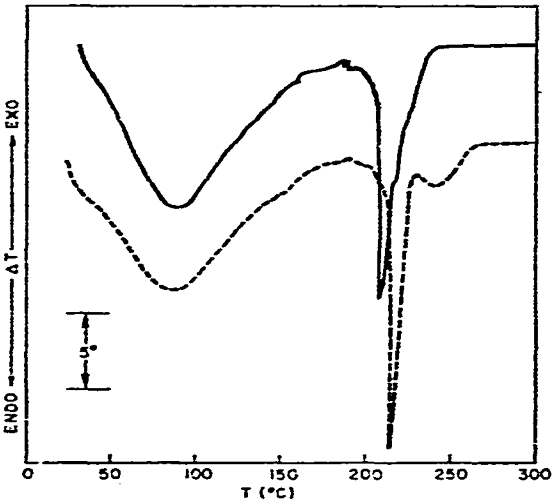

Fig. 2. DTA curves for aqueous $Mn(NO_3)_2$; ———, dry oxygen; ———, wet oxygen.

Evolved gas analysis (EGA)

The drops of the manganese(II) nitrate solution were suspended in a small platinum crucible from a platinum wire within a closed platinum furnace tube. This tube was connected to a Veeco SPI-10 residual gas analyser and the pressure was maintained between 10^{-5} and 10^{-8} torr with a Welsh Turbomolecular pump. The sample was pumped overnight at room temperature prior to starting a run. The furnace surrounding the platinum tube was then programmed to rise at about3 °C/min. The mass range of the analyser was repeatedly scanned between 0 and 55 m.u. and the output recorded, on pen one. The output from a Pt/Pt–Pt–10% Rh thermocouple in close proximity to the sample was simultaneously recorded on pen two of the Bristol Recorder.

Fig. 3 shows a plot of the relative intensity of the pertinent mass peaks as a function of temperature. The mass peaks for NO^+, NO_2^+ and N_2O^+ all behave similarly. The peak corresponding to NO_2^+ is shown in Fig. 3 while the peaks for NO^+ and N_2O^+ which are not shown reach relative intensities of 8.5 and 3.0 on the same scale at the same peak temperature.

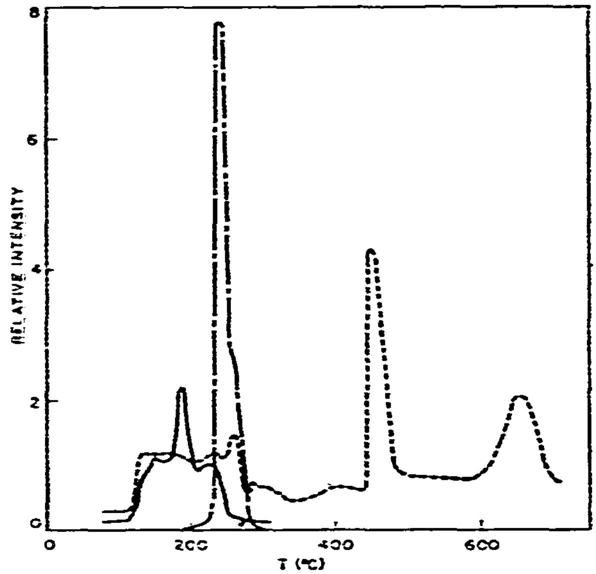

Fig. 3. EGA curves for aqueous $Mn(NO_3)_2$ heated in vacuum; ———, mass 18 (H_2O^+); ----, mass 32 (O_2^+); — — —, mass 46 (NO_2^+).

X-ray, IR and surface area analysis

In an effort to help establish the identity of possible intermediates in the decomposition, 10 ml aliquots of manganese(II) nitrate solution were placed in platinum crucibles and heated in air overnight at 100°C. The furnace temperature was raised to 125°C and a sample removed after 3 h. Thereafter the furnace was raised in increments of 25°C at half hour intervals and a sample removed at the end of each step. X-ray diffraction patterns of these samples were measured using a GE Model XRD-3 diffractometer and Cr$K\alpha$ radiation. The samples heated at 125 and 150°C exhibited no discernible pattern. Those fired at 175 to 250°C gave patterns attributed to δ-MnO_2 and pyrolusite. The amount of the δ-phase steadily diminished from predominant at 175 to minor at 250°C.

A portion of each residue was examined by IR spectroscopy. A Perkin–Elmer Model 412 spectrophotometer was purged with dry nitrogen and used to measure the spectrum from 300–4000 cm^{-1}. The KBr pellet technique was employed and an appropriate KBr pellet was placed in the reference beam. Fig. 4 presents the resulting spectra.

Surface areas of the samples heated to 175–250°C were measured by nitrogen adsorption using the BET technique. There was little variation in the results which were 3.5, 2.5, 2.6 and 3.3 m^2/g for 175, 200, 225 and 250°C residues, respectively.

DISCUSSION

Both the DTG, Fig. 1, and DTA, Fig. 2, clearly indicate at least three distinct reaction zones. In the first zone, 25–125°C, the aqueous solution simply loses water going from approximately $Mn(NO_3)_2 \cdot 12H_2O$ to $Mn(NO_3)_2 \cdot 2H_2O$. There is not a

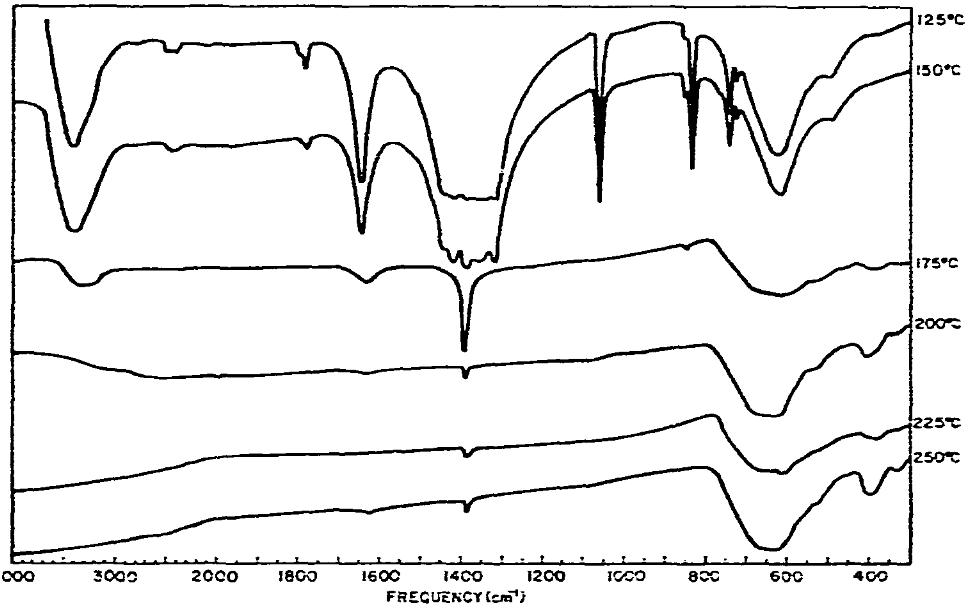

Fig. 4. IR spectra for residues of aqueous $Mn(NO_3)_2$ heated in air.

large water peak in the EGA results, Fig. 3, because the water had been removed by the evacuation overnight. The samples which had been heated at 125–150°C were very hygroscopic and therefore their IR spectra shown in Fig. 4 are not of value in assessing the water content. If the TG run is stopped at a point between the first and second peaks in Fig. 1b, the sample appears as to be a clear pink glass.

Unfortunately, neither the DTG nor DTA curves are able to resolve the next two steps which correspond to the loss of the remaining water and the first step in the nitrate decomposition. Fig. 1a indicates the weight loss levels associated with these two steps. The final weight level chosen in Table II is that corresponding to the appropriate minimum in Fig. 1b. This is obviously not the true value because of differences in reaction rates and the great degree of overlap of the various stages in the decomposition. It is, however, a clearly established point experimentally and therefore was selected to reduce bias. The break in the TG curve at the point corresponding to manganese(III) oxynitrate is also distinct in isothermal kinetic studies[7].

The separation between the initial loss of NO_2 to form manganese(II) oxynitrate and the decomposition of the oxynitrate to form the dioxide is very small indicating very little stability of the oxynitrate. The range of stability is significantly reduced in moist atmospheres as can be seen from the data in Fig. 2 and Table II. The loss of the second molecule of NO_2 occurs more readily due to the catalytic effect of moisture[7]. High vacuum also reduces the separation between the two reactions as shown by the results of the EGA analysis in Fig. 3. Here there is virtually no indication of separate steps except for the very slight shoulder on the NO_2^+ peak at 260–270°C.

The IR spectra in Fig. 4 show the progressive demise of water and nitrate bands and the formation of metal–oxygen bands in the region of 150–200°C. They do not, however, give firm evidence for or against the existence of an oxynitrate intermediate. This is not surprising in view of the anticipated similarity in spectra and the very transient nature of the species. The spectra indicate that nitrite is not an intermediate since there is not even a hint of a prominent nitrite band in the 1230–1250 cm^{-1} region[8].

Traces of nitrate ion persist to higher temperatures or longer times as indicated by both the spectra in Fig. 4 and the prolonged weight loss to 500 °C. This is probably interconnected with the δ-manganese(IV) oxide to pyrolusite transition which is also taking place at these temperatures. The measured surface areas are typical of manganese(IV) oxide prepared in this fashion[9].

The subsequent reductions from MnO_2 to Mn_2O_3 to Mn_3O_4 are all clearly defined in both the TG data, see Fig. 1 and Table II, and in the EGA data presented in Fig. 4. The range of temperature associated with the latter reduction agrees well with the equilibrium data of Hahn and Muan[10] in pure oxygen. As expected, the reductions occur at significantly lower temperatures in nitrogen.

CONCLUSIONS

Several commercially available aqueous solutions of manganese(II) nitrate were found to lose water up to 175–200 °C with the formation of a glassy phase having a composition very near $Mn(NO_3)_2 \cdot 2H_2O$. This material then loses its remaining water and a molecule of NO_2 to form manganese(III) oxynitrate which makes a very transient appearance in the region of 150–270 °C. This composition then loses another molecule of NO_2 to form δ-MnO_2. This material retains traces of nitrate ion to 500 °C and undergoes a structural transformation to the pyrolusite structure. Moisture tends to lower the decomposition temperature of the manganese(III) oxynitrate.

The reductions of the MnO_2 to Mn_2O_3 and then Mn_3O_4 take place below 1000 °C in oxygen and at substantially lower temperatures in nitrogen or vacuum.

REFERENCES

1 W. W. Ewing and C. F. Glick, *J. Amer. Chem. Soc.*, 62 (1940) 2174.
2 W. W. Ewing and H. E. Rasmussen, *J. Amer. Chem. Soc.*, 64 (1942) 1443.
3 W. W. Ewing, C. F. Glick and H. E. Rasmussen, *J. Amer. Chem. Soc.*, 64 (1942) 1445.
4 A. J. Hegedus, K. Horkay, M. Szekely and W. Stefanlay, *Microchim. Acta, 1966*, (1966) 853.
5 P. K. Gallagher and F. Schrey, *Thermochim. Acta*, 1 (1970) 465.
6 P. K. Gallagher and F. Schrey, in R. F. Schwenker, Jr., and P. D. Garn (Eds.), *Thermal Analysis*, Vol. II, Academic Press, New York, 1969, p. 929.
7 P. K. Gallagher and D. W. Johnson, *Thermochim. Acta*, 2 (1971) 413.
8 L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 1958, p. 346.
9 G. V. Malinin and Y. M. Tolmacher, *Russ. J. Phys. Chem.*, 43 (1969) 1129.
10 W. C. Hahn, Jr. and A. Muan, *Amer. J. Sci.*, 258 (1960) 66.