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Note

THERMAL DECOMPOSITION STUDIES ON MANGANESE (III) ACETATE DIHYDRATE

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Manganese (III) acetate ($MnAc_3 \cdot 2H_2O$) is considered to be one of the most stable compounds of manganese (III) and is the starting material for the preparation of several manganese (III) derivatives [1,2]. A survey of the literature shows that no systematic thermal studies of this compound seem to have been carried out so far. We have, therefore, investigated the thermal behaviour of $MnAc_3 \cdot 2H_2O$ separately in air and in nitrogen in detail using DTA, TG and DTG and have interpreted the mode of decomposition.

MATERIALS AND METHODS

$MnAc_3 \cdot 2H_2O$ was prepared by Christensen's method [3], and its purity was checked by analysing manganese iodometrically. Mn found = 20.4%; Mn calculated for $MnAc_3 \cdot 2H_2O = 20.5\%$.

APPARATUS

TG and DTA curves were recorded in an atmosphere of static air on a Stanton recording thermobalance (Model TR01). A heating rate of 4°C min^{-1} and a chart speed of 3 in h^{-1} were employed. A platinum crucible was used for DTA measurements and α-Al_2O_3 was used as reference material. The DTA and TGA experiments in nitrogen atmosphere were carried out on a DuPont 990 thermal analysis system with a model 951 TG analyser and a 1200°C DTA cell using a Pt/Pt–Rh thermocouple. A flow rate of 50 ml min^{-1} of nitrogen and a heating rate of 5° min^{-1} were employed. X-ray powder patterns were taken using a Philips Debye Scherrer camera of diameter 57.3×10^{-2} m using CuK_α radiation ($\lambda = 0.1542$ nm).

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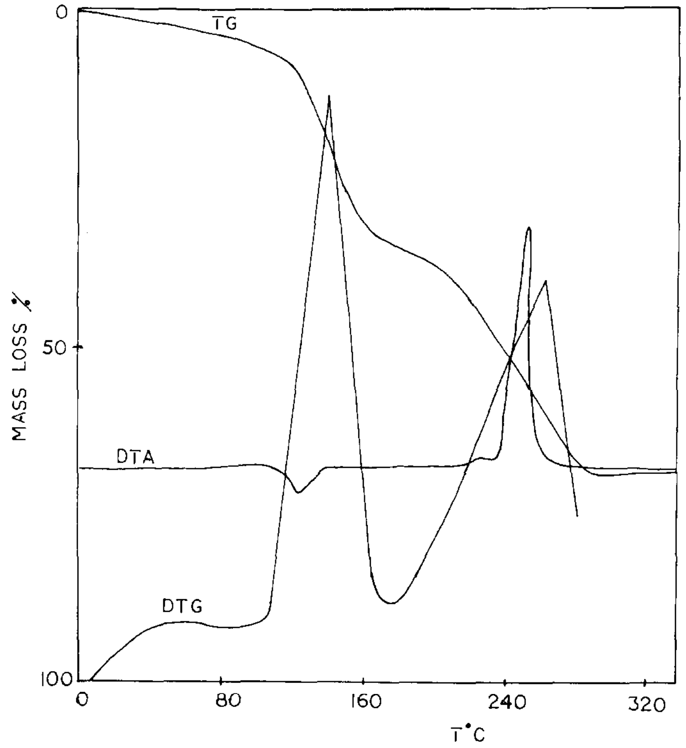

Fig. 1. TG, DTG and DTA curves in air.

The magnetic measurements were made by the Gouy method using Hg[Co(CNS)$_4$] as calibrant. The IR spectrum was recorded on a Perkin-Elmer 221 IR spectrophotometer.

The instrumental TG curve in air was redrawn in the form of mass vs. temperature (TG) curves and rate of mass loss vs. temperature (DTG) curves. The instrumental DTA curves and the TG and DTA curves in nitrogen were used without modification.

RESULTS AND DISCUSSION

TG, DTG and DTA curves are given in Figs. 1 and 2. Peaks, plateaus and stability ranges are given in Table 1. The pyrolytic data are presented in Table 2.

THERMAL BEHAVIOUR

The peak temperatures themselves do not have a great significance since they are dependent on several procedural factors such as sample size, sample mass, heating rate, etc. [4]. Nevertheless, a comparison of the DTG and DTA

TABLE 1

Plateaus, peaks and temperature ranges

Stage	Stability range TG (°C)	Peaks (°C)		Temperature range (°C)	
		DTG	DTA	DTG	DTA
In air					
I	Ambient to 110	144	130 (endo)	110–170	110–160
II		264	255 (exo)	180–300	255–265
In nitrogen					
I	Ambient to 40	70	70	40–90	40–90
II		210	210	100–230	100–240
III		250	260	230–260	240–270
			350		350–370
			390		380–400
			425		410–440

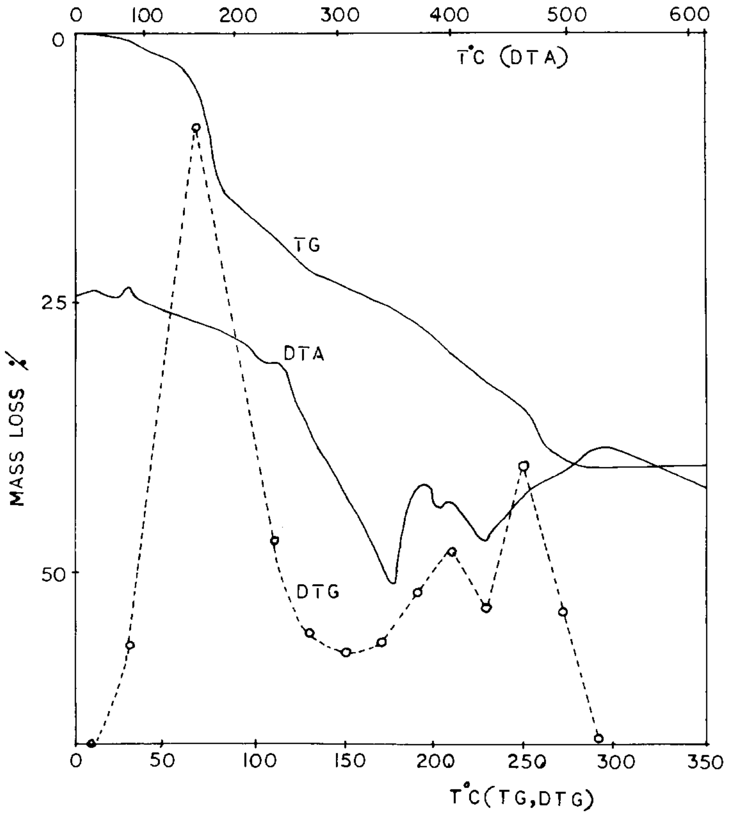

Fig. 2. TG, DTG and DTA curves in nitrogen.

peak temperatures was considered worthwhile. The DTA curves in air show only two peaks, one endothermic peak at 130°C and an exothermic one at 255°C. The corresponding peaks in DTG are at 144 and 264°C, respectively. The agreement is satisfactory. The TG curve in air shows that $MnAc_3 \cdot 2H_2O$ is fairly stable from ambient temperature to 110°C. Above 100°C, the compound starts decomposing fairly rapidly.

The mass loss data from TG show that the residue at the end of stage I of the decomposition corresponds to $Mn(OH)Ac_2$. The mass loss obtained (34%) is higher than the theoretically expected value (29.1%). This may be attributed to the fact that the plateau region in the TG after the first stage of decomposition is very narrow. Probably, the second stage of decomposition commences immediately after the first stage ends. The residue of stage I, viz. $Mn(OH)Ac_2$, obtained from an independent pyrolytic study at 140°C for 10 min was characterised by estimating manganese(III) iodometrically. (Mn found = 32.06%, Mn calculated for $Mn(OH)\ Ac_2 = 28.94\%$.) It was further characterised by magnetic susceptibility measurements and its IR spectrum. The residue shows an effective magnetic moment of 4.2 B.M. This value is lower than the spin-only value expected (4.9 B.M.) for trivalent manganese. The reduction in magnetic moment is tentatively attributable to some metal–metal interaction caused by the bridging hydroxyl group. The presence of OH is confirmed by the IR spectrum. The OH stretch is observed at 3450 cm^{-1}. The M–OH bend present at 1040 cm^{-1} is characteristic of compounds having bridging OH groups [5].

The mass loss in TG after the second stage of decomposition is 66.4% which is in agreement with the independent pyrolysis value of 66.5%. The theoretical mass loss calculated for the decomposition to give a residue of MnO_2 would be 67.5%, whereas that for a residue of Mn_2O_3 would be 70.5%. Thus, the mass loss data would appear to suggest the residue to be MnO_2. However, an X-ray analysis of the product obtained from an independent pyrolytic study at 600°C shows that the residue is Mn_2O_3 (*d* from the data file: 2.72 (100); 1.66 (30); *d* observed: 2.69 (100); 1.68 (30)].

TABLE 2

Pyrolytic data

Stage	Residue	Mass loss%		Theoretical
		TG	Independent pyrolysis	
In air				
I	$Mn(OH)Ac_2$	34.0	34.9	29.1
II	Mn_2O_3	66.4	66.5	70.5
In nitrogen				
I	$Mn(OH)Ac_2$	24	25.1	29.1
II	$Mn_2(CO_3)_3$	50	–	54.1
III	$MnCO_3$	40	–	42.9

The first DTA peak is endothermic as would be expected for decomposition processes in general. The exothermic nature of the second DTA peak (at 225°C) could be explained as due to the concomittant oxidation of some of the decomposition products.

The nature of the DTA curve obtained in an inert atmosphere of nitrogen is totally different from that obtained in air as expected. The DTA curve shows a broad endothermic peak starting at 40°C and extending to 90°C. There are two endothermic peaks at 210 and 260°C. The corresponding peaks in DTG are at 210 and 250°C, respectively. There are three more endothermic peaks in DTA, at 350, 390 and 425°C for which there are no corresponding peaks in DTG. Therefore, the peaks at 350, 390 and 425°C in the DTA curve appear to be due to phase changes.

The mass loss data from TG show that the residue obtained at the end of stage I of decomposition (90°C) in nitrogen corresponds to $Mn(OH)Ac_2$. The mass loss data observed in this case (24%) are slightly lower than the theoretical value (29.1%). In nitrogen atmosphere the elimination of a molecule each of acetic acid and water occurs as is the case in air, but at a lower temperature. The residue was characterised by chemical analysis after an independent pyrolytic study at 90°C for 10 min (Mn observed = 28.35%, calculated = 28.94%, $\mu_{eff} = 4.27$ B.M.). There appears to be a second stage of decomposition in the nitrogen which is not well defined. The residue obtained after the final stage in TG corresponds to 40%. The theoretical value calculated for decomposition to leave a residue of $MnCO_3$ is 42.9%. An independent pyrolytic study at 290°C for 10 min was carried out to characterise the final product. The residue was found to be manganese carbonate by a qualitative analysis.

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REFERENCES

1 C.P. Prabhakaran and C.C. Patel, J. Inorg. Nucl. Chem., 30 (1968) 867.
2 C.P. Prabhakaran and C.C. Patel, J. Inorg. Nucl. Chem., 31 (1969) 3316.
3 O.T. Christensen, Z. Anorg. Chem., 27 (1901) 326.
4 S.R. Dharwadkar and M.D. Karkhanawala, Proc. Int. Conf. Thermal Analysis, Worcester, MA, 1968, Academic Press, New York, 1969, Vol. II, p. 1049.
5 K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1963.