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THERMAL DECOMPOSITION OF MANGANESE(II) BIS(OXALATO)MANGANATE(II) TETRAHYDRATE

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ABSTRACT

Manganese(II) bis(oxalato)manganate(II) tetrahydrate, $Mn[Mn(C_2O_4)_2]\cdot 4H_2O$, has been synthesized and characterized on the basis of elemental analysis, IR, electronic and ESR spectroscopy and magnetic-moment measurements. The low value of μ_{eff} from the spin-only value is indicative of antiferromagnetic spin pairing between two paramagnetic manganese(II) ions and in the metal–metal bond. Thermal decomposition studies (TG, DTG, DTA and DSC) in air, oxygen and nitrogen media showed that completely anhydrous compound was formed at 147, 144 and 138 °C, respectively. The final end product in air and oxygen was Mn_2O_3, whereas in nitrogen a mixture of MnO and MnC_2O_4 formed at ca. 372 °C which finally gave MnO at ca. 416 °C. The activation energies (E^*) of the dehydration and decomposition steps in different media have been calculated and compared with the values found by DSC in air. On the basis of the results, tentative mechanisms of the decomposition have been proposed.

INTRODUCTION

Although, oxalato complexes of transition and non-transition metals of various types have been studied extensively by different workers [1–10], complexes of the type $Mn[Mn(C_2O_4)_n]\cdot XH_2O$ are still unknown. Extensive studies on $K_3Mn(C_2O_4)_3\cdot 3H_2O$ by Simmons and Wendlandt [11] suggested that at 100 °C a white mixture of $K_2C_2O_4$ and $K_2Mn(C_2O_4)_2$ in the molar ratio of 1 : 2 was produced with a mixture of K_2CO_3 and Mn_3O_4 finally being given at ca. 250 °C. Later, Bancroft et al. [12] extended the radiolytic decomposition of the same compound: although the thermal decomposition was almost the same as that reported by Wendlandt et al. [11], the IR spectrum was similar to $K_6(C_2O_4)_2Fe^{(II)}(OX)Fe^{(II)}(C_2O_4)_2$. A detailed study on $K_2[Mn(C_2O_4)_2]\cdot 2H_2O$ has been reported by Nagase et al. [13]. Studies on the fluoroderivatives of the type $A[MnF(C_2O_4)]$ ($A = NH_4$ or K) and $Na[MnF(C_2O_4)]\cdot 2H_2O$ have also been reported [14]. A thermochemical investigation using the DSC of the decomposition of manganese(II) oxalate dihydrate was reported by Brown et al. [15].

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In the present series of studies, a series of oxalato complexes of the type $M[M(C_2O_4)_n] \cdot XH_2O$ [16–19] (where M = same metal) were synthesized. As an extension of this work this paper reports the synthesis, characterization and thermal decomposition kinetics in air, oxygen and nitrogen of the hitherto unknown manganese(II) bis(oxalato)manganate(II) tetrahydrate, $Mn[Mn(C_2O_4)_2] \cdot 4H_2O$. In addition, a tentative mechanism for the decomposition is suggested.

EXPERIMENTAL

Preparation of the complex

Manganese(II) chloride was dissolved in glacial acetic acid and heated on a steam bath. The solution was filtered and a white compound was precipitated by dropwise addition of a hot saturated solution of oxalic acid in glacial acetic acid. The compound was filtered off and purified using standard procedures [16]. The water content of the compound was determined gravimetrically. The manganese content was estimated gravimetrically by precipitating the manganese as $MnNH_4PO_4 \cdot H_2O$. Carbon and hydrogen contents were determined using a Thomas CH analyser. Analysis as calculated for $Mn[Mn(C_2O_4)_2] \cdot 4H_2O$: Mn, 30.70%; C, 13.41%; H, 2.235%; H_2O, 20.11%. Found: Mn, 30.25%; C, 13.30%; H, 2.30%; H_2O, 20%.

Spectroscopic and thermal measurements

Infrared (4000–600 cm^{-1}), far IR, diffuse reflectance and ESR spectra, and magnetic-moments and thermal data (DTA, TG, DTG and DSC) were recorded as described previously [16–19]. The IR spectra of the gases evolved during decomposition were recorded as described previously [16]. The kinetic parameters of the phase-transformation process in DSC were evaluated by the method described by Wendlandt [20].

RESULTS AND DISCUSSION

The complex, $Mn[Mn(C_2O_4)_2] \cdot 4H_2O$, was obtained as a white microcrystalline compound which was insoluble in common organic solvents, but decomposed in strong acid or alkali.

The room-temperature magnetic moment of the compound was 5.42 B.M. The considerable lowering of the μ_{eff} value from the spin-only value suggested the occurrence of a weak antiferromagnetic exchange interaction between adjacent manganese(II) atoms [19,21,23]. The magnetic moment of $K_2[Mn(C_2O_4)_2] \cdot 2H_2O$ was reported previously [22] as 5.90 B.M.

TABLE 1

Selected bands of the IR spectrum of the complex $Mn[Mn(C_2O_4)_2]\cdot 4H_2O$

IR bands [a] (cm^{-1})	Assignments
3000–3700(b)	$\nu_{sy}(O–H) + \nu_{asy}(O–H)$ or hydrogen bonding
1630(s)	$\delta_{sy}(H–O–H)$
1500–1800(b)	$\nu_{asy}(C=O)$
1360(m)	$\nu_{sy}(C–O)$ and/or $\nu(C–C)$
1315(s)	$\nu_{sy}(C–O)$ and/or $\delta(O–C=O)$
815(s)	$\nu(Mn–O)$ and/or $\delta(O–C=O)$
730(b)	Co-ordinated water
600(m)	Crystal water
490(m)[470(sh)]	$\nu(C–C)$ and/or ring deformation
300(m)	Out-of-plane bending
153(ms)	$\nu(Mn–Mn)$

[a] (m) Medium; (s) strong; (b) broad.

The ESR spectrum of the powdered compound at liquid nitrogen temperature gave a g value of 2.01. The electronic spectrum of the solid compound exhibited two d–d bands [21] at 15 620 and 20 400 cm^{-1}. The higher energy bands at 35 000 cm^{-1} may be due to M → L or L → M (where M is the metal and L the ligand) charge transfer and the bands observed at 41 660 and 50 500 cm^{-1} in the ultraviolet region were due to the $\pi \rightarrow \pi^*$ transition [18,19,21].

The analysis of water content revealed four molecules of water per molecule of the compound. The elemental analysis, spectral and magnetic measurement results were consistent with the proposed formula of the complex: $Mn[Mn(C_2O_4)_2]\cdot 4H_2O$.

The low μ_{eff} value and the extreme insolubility of the compound as well as the presence of a sharp peak at 153 cm^{-1} in the far IR spectrum is indicative of the presence of a metal–metal bond [17–19,24]. The IR spectral data (Table 1) suggested a chelating nature of the oxalato group as well as the presence of co-ordinated water molecule [25].

The DTA curves (Figs. 1 and 2) showed an endothermal change in the temperature range 116–190 °C ($\Delta T_{min} = 150$ °C) in air and in the range 100–170 °C ($\Delta T_{min} = 133$ °C) in oxygen. Large exothermic peaks were seen with ΔT_{max} values of 297 °C in air and 293 °C in oxygen. A small exothermal hump was seen in the temperature range 400–480 °C ($\Delta T_{max} = 443$ °C) and 410–490 °C ($\Delta T_{max} = 457$ °C) in air and oxygen, respectively.

The TG curves showed that the compound was stable up to 117 °C in air and 112 °C in oxygen (Figs. 1 and 2). Above these temperatures the compound started to lose weight until 147 °C (in air) and 144 °C (in oxygen) with a weight loss of 19.80% (calculated 20.11%). These weight losses indicate the formation of an anhydrous compound. The endothermic peaks

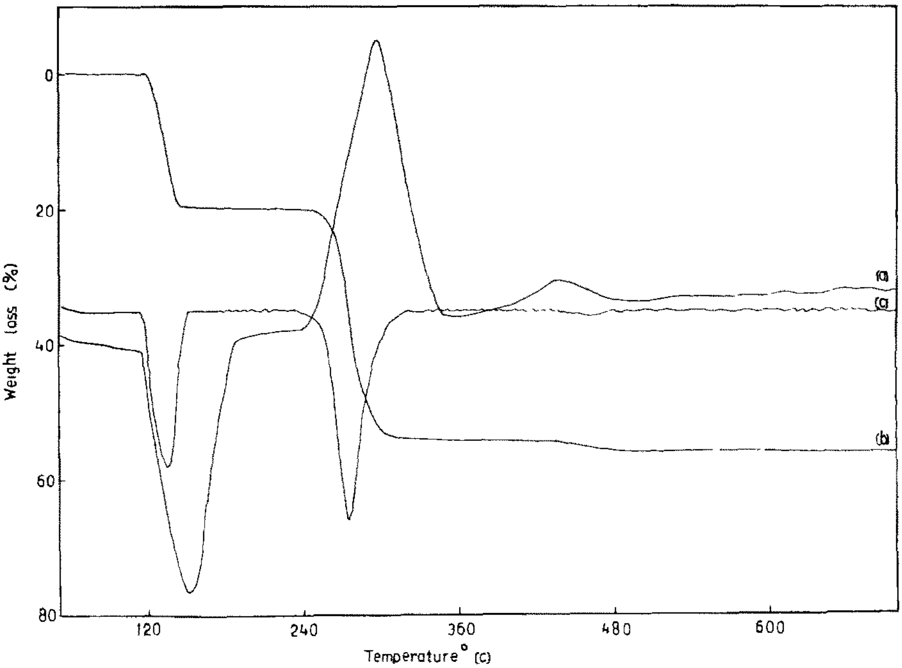


Fig. 1. (a) DTA, (b) TG and (c) DTG curves of $Mn[Mn(C_2O_4)_2]\cdot 4H_2O$ in air.

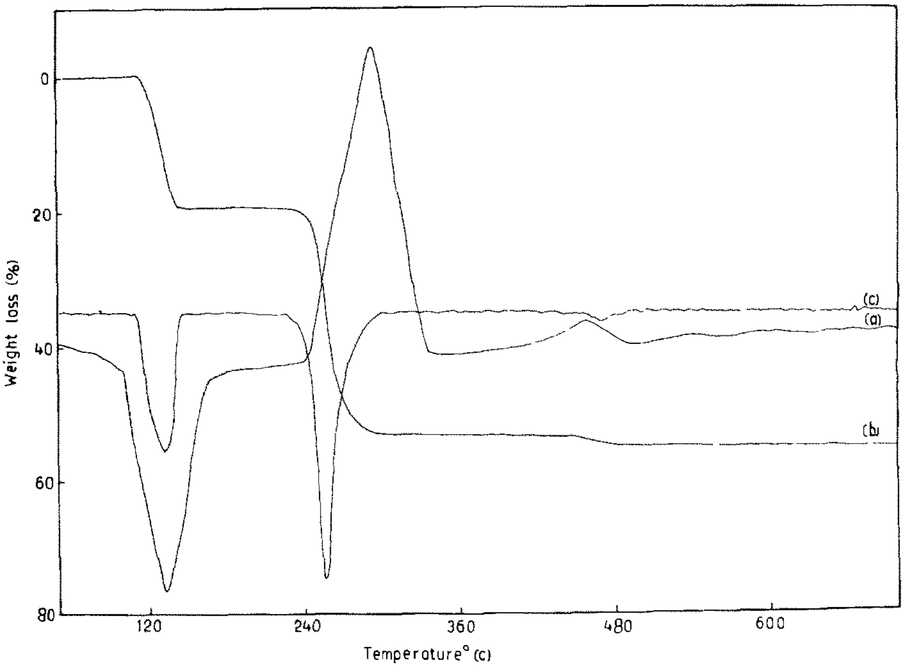


Fig. 2. (a) DTA, (b) TG and (c) DTG curves of $Mn[Mn(C_2O_4)_2]\cdot 4H_2O$ in oxygen.

at 150 °C (in air) and 133° C (in oxygen) in the DTA curves account for the dehydration process. These peaks corresponded to the DTG peaks at 114–150 °C (in air) and 108–147 °C (in oxygen). The TG curve for the nitrogen medium showed a weight beginning at 111° C and increasing upto 138° C with a total weight loss of 20%. The presence of a DTG peak at 103–144° C indicated the formation of the complete anhydrous compound. An endothermic peak at 100–180 °C ($\Delta T_{mın} = 133°$ C) in the DTA curve was due to this dehydration. The anhydrous compound was almost stable up to 246, 230 and 281° C in air, oxygen and nitrogen, respectively.

The compound was isolated by the temperature-arrest technique and the chelating character of the oxalato group was concluded from the IR spectrum [26]. On exposure to humid atmosphere the original compound was reformed as evidenced by the presence of a broad band in the 3000–3700 cm^{-1} region of the IR spectrum of the rehydrated complex. The activation energies (E^*) of this dehydration stage in the three media were calculated using Freeman and Carroll's technique [27] and were found to be 136.75, 60.46 and 66.57 kJ mol^{-1} in air, oxygen and nitrogen, respectively. This dehydration stage was evident in the DSC (air) curves by endothermic peaks at 120–160 °C ($\Delta T_{min} = 144.5$ °C) and 122–175 °C ($\Delta T_{mın} = 151.7$ °C) for heating rates of 5 and 10 °C min^{-1}, respectively. The kinetic parameters, activation energies (E^*), enthalpy changes (ΔH), the logarithm of pre-exponential factors ($\ln k_0$) and the order of reaction are tabulated in Table 2.

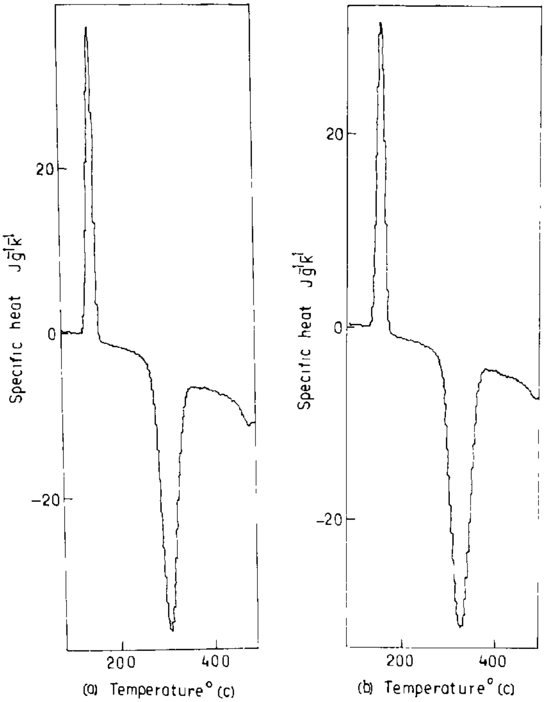
The breakdown of the anhydrous compound was shown in the TG curve to take place beyond 246 °C (in air) and 230 °C (in oxygen) and the slope upto 314° C and 296 °C with the weight losses of 54.35% (in air) and 53.58% (in oxygen), respectively, indicated the formation of Mn_2O_3. The calculated weight loss for this stage was 55.88%. The exothermic peaks in the DTA curve at 297 °C (in air) and 292.7 °C (in oxygen) and in the DTG curve at 238–351° C (in air) and 225–300 °C (in oxygen) indicated these decomposition processes.

The end product thus formed was stable upto 435 °C (in air) and 441° C (in oxygen) beyond which temperatures the weight losses of 1.3% (in air) and 1.36% (in oxygen) and the overall weight losses of 55.65% (in air) and 54.95% (in oxygen) were observed. The residue was shown by the TG curve to be stable upto 700 °C. The small exothermic peaks at 443° C (in air) and 457 °C (in oxygen) were due to this weight loss. The estimated manganese content (found, 69%; calculated 69.59%), the presence of bands at 610s, 490s, 400w and 350w cm^{-1} in the IR spectrum of the end product, and the concomitant weight loss shown by TG curve indicated the compound to be Mn_2O_3. The E^* values of this decomposition stage were calculated as 114.88 (in air) and 202.11 kJ mol^{-1} (in oxygen), whereas the values supplemented by DSC in air were 220.33 ± 13.44 (5 °C min^{-1}) and 184.72 ± 12.86 kJ mol^{-1} (10 °C min^{-1}). The exothermic peaks in the range 255–350 °C ($\Delta T_{max} = 303.1$° C) at 5 °C min^{-1} and 260–380 °C ($\Delta T_{max} = 325.7$ °C) at 10 °C min^{-1} heating rates in DSC accounted for this decomposition.

TABLE 2

The DSC data of $Mn[Mn(C_2O_4)_2]\cdot 4\ H_2O$ in air

Heating rate (°C min^{-1})	Step	T (°C)	T_{max} (°C)	Weight loss (%)		ln k_0	E^* (kJ mol^{-1})	ΔH ($\times 10^4$ kJ mol^{-1})	Order of reaction	Reaction
				Found	Calc.					
5	1	120–160 (endo.)	144.5	19.83	20.11	65.01 ± 1.53	240.44 ± 5.19	20.95	0.95 ± 0.03	Dehydration
	2	255–350 (exo.)	303.1	54.65	55.88	40.84 ± 2.89	220.33 ± 13.44	35.19	1.57 ± 0.11	Decomposition
10	1	122–175 (endo.)	151.7	19.27	20.11	62.99 ± 1.7	235.62 ± 5.87	20.53	1.12 ± 0.04	Dehydration
	2	260–380 (exo.)	325.7	55.74	55.88	32.44 ± 2.67	184.72 ± 12.86	36.87	1.39 ± 0.11	Decomposition



(a) Temperature° (c)

(b) Temperature° (c)

Fig. 3. Plot of specific heat (C_p) values versus temperature at heating rates of (a) 5 ° C min^{-1} and (b) 10 ° C min^{-1}.

Other kinetic parameters are also listed in Table 2. The weight losses of 54.65% and 55.74% for the annealed sample at 500 ° C at heating rates of 5 and 10 ° C min^{-1}, respectively, were observed. Scanning at different heating rates indicated that the higher the heating rate, the higher the temperature of decomposition. A plot of the specific heat (C_p) versus temperature (Fig. 3) recorded at 5 and 10 ° C min^{-1} indicates a similar transition as that shown in the DSC traces [18]. The plot of α (fraction of the reaction completed) versus time (t) at three different temperatures for each transition were also recorded (Fig. 4).

The TG curve of the anhydrous compound in nitrogen showed that the compound was almost stable up to 281°C (Fig. 5). Above 281°C the compound lost weight until 416 ° C. The anhydrous compound decomposed in two stages as evidenced by the presence of two overlapping DTG peaks in the range 273–422° C with peak temperatures of 327° C and 392° C. The first stage corresponded to the weight loss (found 40%; calculated 40.23%) at ca. 372° C, assuming the mixture to be MnO and MnC_2O_4. It was difficult to isolate the compound as MnC_2O_4 immediately decomposed to the oxide. Fused MnO probably accelerates the decomposition of MnC_2O_4. The inclined nature of the TG curve ended at 416 ° C showing a weight loss of 60.41% (calculated 60.35%) which indicates the formation of 2MnO.

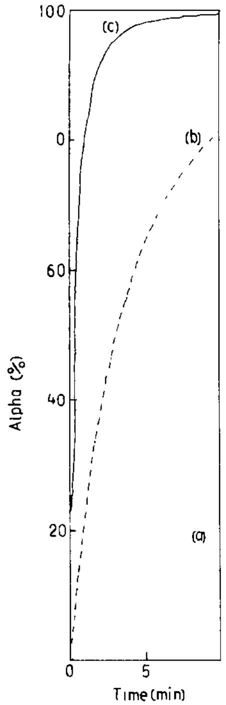


Fig. 4. Plot of α (the fraction of the reaction completed) versus time (t) of $Mn[Mn(C_2O_4)_2] \cdot 4H_2O$ (5 °C min^{-1}) at (······) 270 °C, (·—·—·) 300 °C and (———) 330 °C.

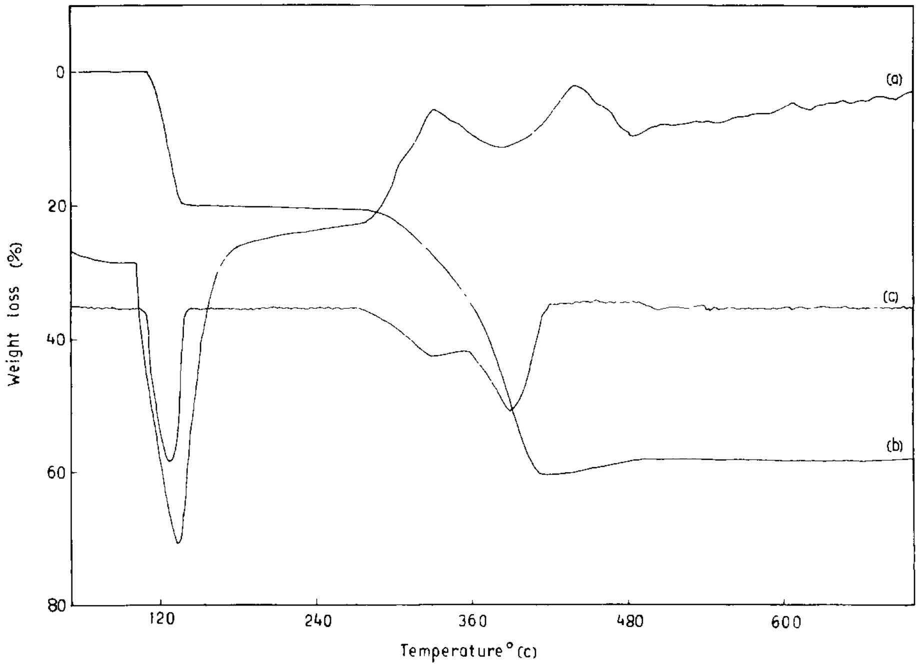


Fig. 5. (a) DTA, (b) TG and (c) DTG curves of $Mn[Mn(C_2O_4)_2] \cdot 4H_2O$ in nitrogen.

Corresponding to this two-stage decomposition, the DTA results showed an exothermic peak at 280–482°C with two ΔT_{max} at 332°C and 440°C; beyond 482°C the exothermic nature of the curve indicated weight gain. The rise in the TG curve beyond 416°C and the stabilization around 495°C with a gain of weight of 2.35% and an overall weight loss of 58.06%, might be due to the presence of carbon formed during disproportionation of CO(g) to CO_2(g) and C [17,19,28], to the evolution of a small excess of CO_2, or to some reduction of MnO which is pyrophoric in nature [15,29]. The E^* of the overall decomposition stage was calculated to be 33.77 kJ mol^{-1}.

The water vapour, carbon monoxide and carbon dioxide evolved during decomposition were identified by IR spectroscopy [25].

On the basis of the above results, the tentatively proposed mechanisms of the three thermal decomposition processes may be summarized as

in air

$$\mathrm{Mn[Mn(C_2O_4)_2]\cdot 4H_2O \xrightarrow{117-147\,^\circ C} Mn[Mn(C_2O_4)_2](s) + 4H_2O(v)}$$

$$\mathrm{\xrightarrow{246-314\,^\circ C} Mn_2O_3(s) + 3CO(g) + CO_2(g) \xrightarrow{\geq 474\,^\circ C} Mn_2O_3(s)\ (stable)}$$

in oxygen

$$\mathrm{Mn[Mn(C_2O_4)_2]\cdot 4H_2O \xrightarrow{112-144\,^\circ C} Mn[Mn(C_2O_4)_2](s) + 4H_2O(v)}$$

$$\mathrm{\xrightarrow{230-296\,^\circ C} Mn_2O_3(s) + 3CO(g) + CO_2(g) \xrightarrow{\geq 480\,^\circ C} Mn_2O_3(s)\ (stable)}$$

in nitrogen

$$\mathrm{Mn[Mn(C_2O_4)_2]\cdot 4H_2O \xrightarrow{111-138\,^\circ C} Mn[Mn(C_2O_4)_2](s) + 4H_2O(v)}$$

$$\mathrm{\xrightarrow{\sim 372\,^\circ C} MnO(s) + MnC_2O_4(s) + CO(g) + CO_2(g)}$$

$$\mathrm{\xrightarrow{ca.\ 416\,^\circ C} 2MnO(s) + CO(g) + CO_2(g) \xrightarrow{\geq 495\,^\circ C} 2MnO(s) + C(s)}$$

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