Thermochimica Acta, 33 (1979) 355—361
© Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

Note

THERMAL DECOMPOSITION STUDIES ON MANGANESE(III) SELENITES

B.L. KHANDELWAL and S.P. MALLELA

Department of Chemistry, Indian Institute of Technology, New Delhi-110029 (India)

(Received 5 December 1978)

Although a number of investigations have been reported [1—6] on the thermal behaviour of various metal selenites, manganese(III) selenites have received very little attention. The present communication deals with the preparation and thermal behaviour of manganese(III) selenites.

EXPERIMENTAL

All the chemicals used were of Analar grade.

Preparation

(1) Manganese(III) selenite tetrahydrate, $Mn_2(SeO_3)_3 \cdot 4\ H_2O$

3.33 g of selenium dioxide were dissolved in 100 ml of 50% acetic acid and warmed at 60°C. A solution of 2.68 g of manganese(III) acetate dihydrate in 100 ml hot glacial acetic acid when slowly added to the above solution with constant stirring gave a dark brown product. It was digested on a water bath for 10 min, filtered and washed subsequently with 50% acetic acid, methanol and ether.

(2) Manganese(III) hydrogen selenite, $MnH(SeO_3)_2$

5.36 g manganese(III) acetate dihydrate when treated with 13.32 g of selenium dioxide in acetic acid as mentioned above gave an amber yellow product. It was filtered, washed with methanol and ether.

(3) Ammonium diselenito manganese(III) monohydrate, $NH_4Mn(SeO_3)_2 \cdot H_2O$

15.4 g of ammonium acetate were added to 20 g of selenium dioxide dissolved in 50 ml distilled water. To this solution (pH ≈ 3.5) 1.2 g of manganese(III) selenite tetrahydrate was added and stirred vigorously for 2—3 min. The undissolved selenite was separated. The clear brownish pink solution gave dark brown crystals on keeping overnight.

(4) Potassium diselenito manganese(III) sesquehydrate, $KMn(SeO_3)_2 \cdot 1.5\ H_2O$

20 g of potassium acetate and 20 g of selenium dioxide were added to 50

TABLE 1

Analytical and magnetic results

Compound	Manganese (%)		Selenium (%)		Water (%)		Alkali (%)		μ_{eff} BM
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	
$Mn_2(SeO_3)_3 \cdot 4\ H_2O$	19.54	20.02	42.10	41.98	12.79	12.00	—	—	4.94
$MnH(SeO_3)_2$	17.74	17.36	50.94	51.20	—	—	—	—	4.85
$(NH_4)Mn(SeO_3)_2 \cdot H_2O$	15.94	16.12	45.77	45.92	5.70	5.50	5.22	4.98	4.99
$KMn(SeO_3)_2 \cdot 1.5\ H_2O$	14.66	15.02	42.11	41.91	7.20	7.50	10.43	11.01	4.98

ml distilled water. This solution (pH ≈ 3.5) was treated with manganese(III) selenite tetrahydrate exactly as mentioned above to obtain deep brown crystals.

Analysis

Manganese was estimated spectrophotometrically as permanganate after the removal of selenium. Selenium was weighed in the elemental form after reduction with sulphurous acid from solutions of compounds in concentrated HCl. Potassium was determined by the tetraphenyl boron method and also by micro determination of nitrogen. Analytical data have been compiled in Table 1.

Magnetic susceptibilities were determined with a Cahn Faraday Electromagnetic balance with $Hg[Co(NCS)_4]$ as standard. TGA study was carried out on a Stanton recording thermobalance, model HT-D. DTA study was made with Stanton Red Craft DTA 673-4 unit.

RESULTS AND DISCUSSION

The effective magnetic moments of these compounds measured at room temperature (Table 1) correspond to the value 4.9 BM required for a high spin d^4 ion without orbital contribution. This clearly confirms the trivalent state of manganese in all the compounds.

Thermoanalytical curves (Figs. 1—4) of these compounds revealed several changes on heating. All compounds lose water only above 140°C except compound (4) where half a mole is lost at 80°C. The weight loss and the corresponding endothermic effect suggest the loss of water. IR spectra of compounds heated at 200°C to a constant weight showed the absence of water. The decomposition process of manganese(III) hydrogen selenite closely resembles that of iron(III) hydrogen selenite [7]. In the case of ammonium diselenito manganese(III) the loss in the range 280—380°C corresponds to the elimination of ammonia which is confirmed by the IR spectrum of the heated samples. A significant weight loss around 400°C in all the compounds indicates the formation of manganese(III) oxyselenite. The decomposition of anhydrides to oxyselenites clearly indicates the transient existence of intermediates as is evident from slight inflexion points instead of horizontal levels in TG curves. The corresponding DTA peaks account for the endothermic effect during this decomposition. Between 440 and 620°C, manganese(III) oxyselenite, except in the case of compound (4), is converted to Mn_2O_3. The endothermic peak at the corresponding temperature is associated with this change.

The thermal behaviour of potassium diselenito manganese(III) sesquehydrate (Fig. 4) appears to be somewhat different from that of other compounds. Besides showing endothermic peaks for loss of water and formation of oxyselenite, it shows an exothermic effect at 340°C without any weight loss. This could be attributed to some structural transformation. The formation of K_2SeO_3 at this stage has been ascertained by extracting the heated

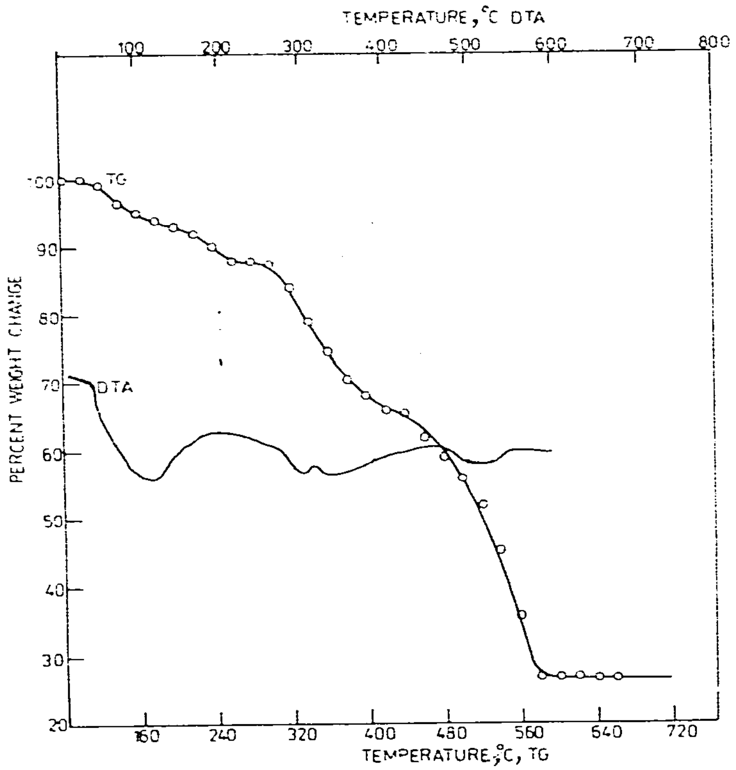

Fig. 1. TG—DTA of $Mn_2(SeO_3)_3 \cdot 4\ H_2O$.

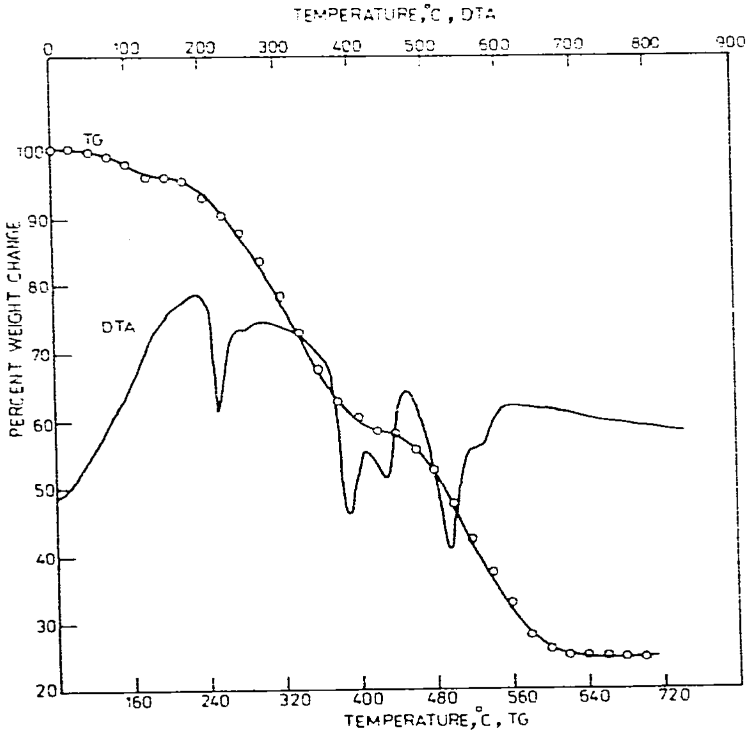

Fig. 2. TG—DTA of $MnH(SeO_3)_2$.

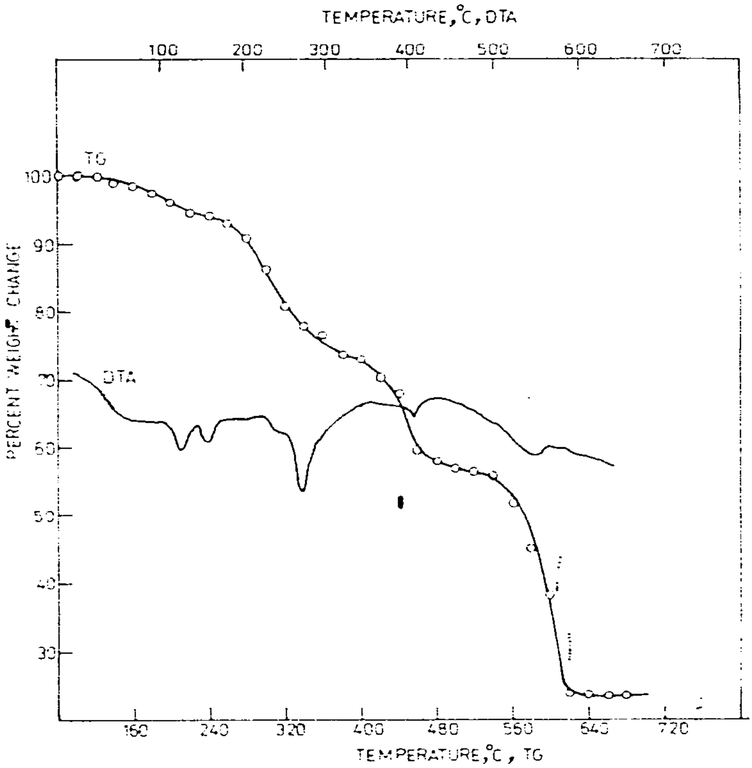

Fig. 3. TG—DTA of $NH_4Mn(SeO_3)_2 \cdot H_2O$.

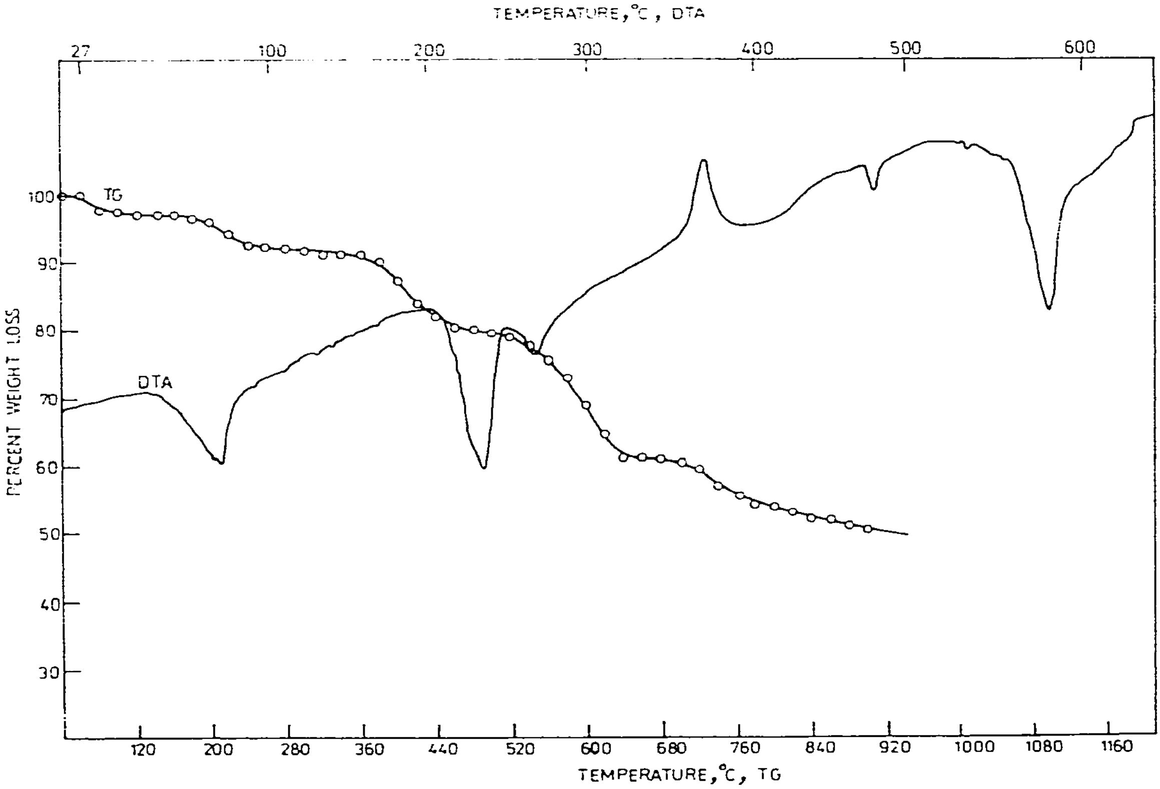

Fig. 4. TG—DTA of $KMn(SeO_3)_2 \cdot 1.5\ H_2O$.

TABLE 2

Thermo-analytical results of manganese(III) selenites

	Dehydration/decomposition transition	Temp. (°C)		Loss (%)	
		TG	DTA	Calc.	Found
(1)	*$Mn_2(SeO_3)_3 \cdot 4\,H_2O$*				
	$Mn_2(SeO_3)_3 \cdot 4\,H_2O \rightarrow Mn_2(SeO_3)_3$	140—260	115 Endo 290 Endo	12.7	12.0
	$Mn_2(SeO_3)_3 \rightarrow Mn_2O(SeO_3)_2$	300—440	430 Endo	32.5	34.0
	$Mn_2O(SeO_3)_2 \rightarrow Mn_2O_3$	440—620	530 Endo	71.9	73.0
(2)	*$MnH(SeO_3)_2$*				
	$2\,MnH(SeO_3)_2 \rightarrow Mn_2(SeO_3)_3SeO_2$	160—210	215 Endo	2.9	3.8
	$Mn_2(SeO_3)_3SeO_2 \rightarrow Mn_2O(SeO_3)_2$	220—440	390 Endo 440 Endo	38.7	41.6
(3)	*$Mn_2O(SeO_3)_2 \rightarrow Mn_2O_3$*				
	$NH_4Mn(SeO_3)_2 \cdot H_2O$	440—620	525 Endo	74.5	75.0
	$2\,NH_4Mn(SeO_3)_2 \cdot H_2O \rightarrow 2\,NH_4Mn(SeO_3)_2$	160—240	120 Endo 160 Endo	5.7	6.0
	$2\,NH_4Mn(SeO_3)_2 \rightarrow Mn_2(SeO_3)_3$	280—380	260 Endo	28.8	26.5
	$Mn_2(SeO_3)_3 \rightarrow Mn_2O(SeO_3)_2$	400—500	400 Endo	44.8	43.0
	$Mn_2O(SeO_3)_2 \rightarrow Mn_2O_3$	520—620	550 Endo	77.01	76.2
(4)	*$KMn(SeO_3)_2 \cdot 1.5\,H_2O$*				
	$2\,KMn(SeO_3)_2 \cdot 1.5\,H_2O \rightarrow 2\,KMn(SeO_3)_2H_2O$	60—80	77 Endo	2.4	2.5
	$2\,KMn(SeO_3)_2 \cdot H_2O \rightarrow 2\,KMn(SeO_3)_2$	220—260	227 Endo	7.2	7.5
	$2\,KMn(SeO_3)_2 \rightarrow K_2SeO_3 + Mn_2O(SeO_3)_2$	360—460	267 Endo 340 Exo	21.9	20.0
	$K_2SeO_3 + Mn_2O(SeO_3)_2 \rightarrow K_2SeO_3 + Mn_2O_2(SeO_3)$	480—640	470 Endo	36.7	38.5
	$K_2SeO_3 + Mn_2O_2(SeO_3) \rightarrow Mn_2O_3 + K_2SeO_3$	640—840	580 Endo	50.26	48.0

(340°C) sample and analysing the aqueous extract for potassium and selenium. The oxyselenite in this case appears to decompose above 480°C and the weight loss at 640°C corresponds to the formation of manganese(III) dioxyselenite which is not observed in the other compounds. The formation of dioxyselenite has, however, been observed [8,9] during the thermal decomposition of rare earth selenites. On further heating to 840°C the dioxyselenite decomposes to Mn_2O_3.

Thermoanalytical results of manganese(III) selenites and the proposed decomposition transition processes are summarised in Table 2.

CONCLUDING REMARKS

The present thermal investigations on manganese(III) selenites showed interesting decomposition mechanisms. All selenites decompose to manganese(III) oxyselenite around 400°C. The oxyselenite formed in the case of potassium diselenito manganese(III) sesquehydrate is converted into dioxyselenite. Finally, the decomposition proceeds to the formation of manganese(III) sesqueoxide.

REFERENCES

1 R.Y. Melnikova, V.N. Makatun, V.V. Pechkovskii, A.K. Potapovich and V.Z. Drapkin, Zh. Neorg. Khim., 23 (1978) 691.
2 R. Frydrych, Z. Anorg. Allg. Chem., 427 (1976) 260.
3 J. Tudo and D. Jolibois, C. R. Acad. Sci., 283 (1976) 469.
4 A.S. Znamenskaya, L.N. Komissarova and V.M. Shatskii, Zh. Neorg. Khim., 22 (1977) 2124.
5 M. Koskenlinna, L. Niinistö and J. Valkonen, Acta Chem. Scand., Ser. A, 30 (1976) 836.
6 B.L. Khandelwal and V.P. Verma, J. Inorg. Nucl. Chem., 38 (1976) 763.
7 G.F. Pinaev, V.V. Pechkovskii and V.P. Volkova, Russ. J. Inorg. Chem., 15 (1970) 1060.
8 A.S. Znamenskaya and L.N. Komissarova, Zh. Neorg. Khim., 18 (1973) 873.
9 Y.L. Suponitskii, A.I. Maier, V.Y. Kryuchkova and M.K. Karapetyants, Tr. Mosk. Khim. Tekhnol Inst. 54 (1967) 27; Chem. Abstr., 68 (1967) 45872f.