Thermochimica Acta, 71 (1983) 193–197
Elsevier Science Publishers B V , Amsterdam – Printed in The Netherlands

Note

THERMAL ANALYSES OF $Mn(RSO_3)_2$ HYDRATES AND PYRIDINE COMPLEXES ($R = CH_3$, p-$CH_3C_6H_4$, p-ClC_6H_4)

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(Received 1 June 1983)

DTA has been used extensively for evaluation of enthalpies of reactions initiated by heating [1]. Paul et al. [2] have evaluated the enthalpies of deligation of some methylsulphatopyridine cadmium(II) complexes. The present study has been undertaken to evaluate the relative performance of hydrates and pyridine complexes of some manganese(II) derivatives with a view to evaluating their utility for energy storage applications.

Energy storage density is one of the most important criteria for evaluating the suitability of phase-change materials in energy storage applications. Thermogravimetric studies on salt hydrates show that most of the hydrated salts lose their water of crystallization even with small changes in temperature [3] above their melting points. This change in temperature is desirable to reduce the fill-in time so as to compensate for the inherent low thermal conductivity of salt hydrates. The performance of pyridine complexes may be favourable due to the stronger Lewis basicity of pyridine compared with that of water [4].

EXPERIMENTAL

Manganese(II) salts of sulphonic acids were obtained by neutralising manganese(II) carbonate with the acid in aqueous medium. The solution was filtered and the hydrated salt was obtained by crystallization from water The adhering water was removed by pressing the crystals between layers of filter paper and then dried in air for about 48 h at room temperature. The analytical data are presented in Table 1.

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0040-6031/83/$03 00

TABLE 1

Analytical data of some manganese(II) compounds

Compound	Mn		C		H		N		S	
	Found(%)	Calcd (%)	Found(%)	Calcd (%)	Found(%)	Calcd (%)	Found(%)	Calcd (%)	Found(%)	Calcd (%)
$Mn(CH_3C_6H_4SO_3)_2$	13.72	13 83	42 00	42 28	3 33	3.52			16.00	16 13
$Mn(CH_3C_6H_4SO_3)_2$ 7 H_2O	10.31	10 49	31 87	32 09	5 12	5.34			12.19	12 24
$Mn(CH_3C_6H_4SO_3)_2$ 4 py	7 13	7.69	56 55	57 15	4.64	4.76	7 96	7 84	8 83	8.98
$Mn(CH_3SO_3)_2$	22 10	22.40	29 62	29 79	2.12	2.44			26 18	26.15
$Mn(CH_3SO_3)_2$ 4 H_2O	16 98	17 32	7 31	7 56	4.21	4.41			20 10	20.21
$Mn(CH_3SO_3)_2 \cdot 4$ py	9.36	9 78	46 83	47 00	4 73	4 62	9 82	9 97	11 32	11.41
$Mn(p\text{-}ClC_6H_4SO_3)_2$	12.21	12 54	32 13	32 86	1.71	1 82			14 43	14.63
$Mn(p\text{-}ClC_6H_4SO_3)_2$ 2 H_2O	11.41	11 58	29 99	30 36	2 49	2 53			13 71	13.52
$Mn(p\text{-}ClC_6H_4SO_3)_2 \cdot 2$ py	8.99	9.21	44 11	44 26	3 00	3.01	4 52	4 69	10 61	10 75

The anhydrous salts were obtained by dehydrating the hydrates at 120°C in vacuo for about 48 h. The pyridine complexes were obtained by refluxing the anhydrous salts with pyridine for about 10 h and then precipitated with solvent ether. These were repeatedly washed with solvent ether and then dried in vacuo and analysed (Table 1).

The DTA/TG/DTG were run at a heating rate of 5° min^{-1} on a derivatograph, Paulik, Paulik and Erdey (MOM, Budapest) using calorimetric crucibles. The DTA endotherms were calibrated using benzoic acid. The kinetic data were obtained from the TG curves by the method of Zsako [5]. The temperature calibration of the equipment was carried out using benzoic acid, potassium nitrate and silver nitrate [1].

RESULTS AND DISCUSSION

Manganese(II) high-spin compounds have no stability due to CFSE and the Mn^{2+} ion can be considered to have a spherical symmetry [4]. $Mn(CH_3SO_3)_2$ has been assigned an octahedral arrangement with six oxygen atoms around the manganese(II), due to the multidentate character of the CH_3SO_3 group [6]. The spectral and magnetic studies [7] of manganese(II) *p*-tolyl and *p*-chlorophenyl sulphonates indicate that these are also octahedral systems due to the presence of a similar moiety, viz. $-SO_3$. Their hydrates and pyridine complexes have chromophores of types $Mn[O_2{}^*O_4]$ and $Mn[O_2{}^*N_4]$ (where O* is an oxygen atom from the $-SO_3$ group, O is an oxygen atom from an H_2O molecule, and N is a ligating nitrogen atom from a pyridine molecule).

TG measurements

The TG and DTA data of the manganese(II) compounds are tabulated in Table 2. The activation energy and order of reaction were found by Zsako's method [5] as this method eliminates the error due to slope determination. The calculations were carried out on a DEC 2050 machine. The values of the integral, $\int(e^{-u}/u^2)du$, where $u = E/RT$, were calculated by Simpson's method and the values so obtained were found to be quite close to those given by Zsako [5] (± 0.001). The B_n values are also given in Table 2. The dihydrate and bis(pyridine) complex of $Mn(p\text{-}ClC_6H_4SO_3)_2$ have a single step decomposition leading to the formation of the anhydrous salt. However, no attempts were made to isolate the intermediate compounds.

DTA measurements

$Mn(p\text{-}CH_3C_6H_4SO_3)_2 \cdot 7\ H_2O$ and $Mn(CH_3SO_3)_2 \cdot 4\ H_2O$ exhibit an endotherm corresponding to a phase transition as the TG curve shows no

TABLE 2

TG/DTA data of manganese(II) complexes

Compound	ΔTmin (°C)	ΔH (kcal mole^{-1})	$\Delta \overline{H}/m$ (kcal mole^{-1})	E_{act} (kcal mole^{-1})	B_n $\times 10^2$	n	No of ligand molecules lost	Wt loss (%)	
								Found	Calcd
$Mn(CH_3C_6H_4SO_3)_2$ 7 H_2O		2.5					0		
$Mn(CH_3C_6H_4SO_3)_2 \cdot 7$ H_2O	68 5	9.7		13 0	0 3100	1/3	2	7 55	6 97
$Mn(CH_3C_6H_4SO_3)_2 \cdot 5$ H_2O [a]	107 0	4.46	4 7/3				1	11.04	10 46
$Mn(CH_3C_6H_4SO_3)_2$ 4 H_2O [a]	156.3	48.9	12 2/4	55.0	11.032	1	4	24 41	24 41
$Mn(CH_3C_6H_4SO_3)_2$ 4 py	110.8	31.8 [b]		13.5	0 5704	0	2	23 12	22.16
$Mn(CH_3C_6H_4SO_3)_2 \cdot 2$ py [a]	142.2	29 2 [b]	15.2/4	60 0	4 9016	2	2	44.89	44.32
$Mn(CH_3SO_3)_2$ 4 H_2O		1.5					0		
$Mn(CH_3SO_3)_2 \cdot 4$ H_2O	68.7	7 1		16 0	0 3597	1	1 33	7 38	7 55
$Mn(CH_3SO_3)_2$ 2.7 H_2O [a]	109 7	1.8					0.66	10.23	11 31
$Mn(CH_3SO_2)_2$ 2 H_2O [a]	155.6	42.7	12 9/4	51 0	0.1908	1/3	2	23 29	22 80
$Mn(CH_3SO_3)_2 \cdot 4$ py	88.5	7 5		12 0	0 6295	0	1 5	19 86	21 12
$Mn(CH_3SO_3)_2$ 2 5 py [a]	126.8	32 7	10 0/4	67.0	4.8836	2	2 5	56 09	56 80
$Mn(ClC_6H_4SO_3)_2 \cdot 2$ H_2O	132 3	30 4	15 2/2	14 5	2 074	1/3	2	8 64	7.56
$Mn(ClC_6H_4SO_3)_2 \cdot 2$ py	147 7	23.9	11 9/2	22 0	1 992	2/3	2	26.50	26 51

[a] Not isolated

[b] Closely placed DTA endotherms which were resolved graphically.

weight loss. It is proposed that in the heptahydrate three water molecules are present as 'lattice water'. A quantity $\Delta\overline{H}$ has been defined as $\Sigma\Delta H_s/m$, where s is the number of steps in the thermogram and m is the total number of ligand/solvent molecules lost over the various steps. Accordingly, $\Delta\overline{H}$ for H_2O(lattice) comes out to be 4.7 kcal mole^{-1} while the value for H_2O(ligand) is 12.2 kcal mole^{-1}. $\Delta\overline{H}$ values for other systems are shown in Table 2. It is observed that, in general, $\Delta\overline{H}$ for water is higher than that for pyridine.

Since the anhydrous salts have $[MnO_6^*]$ chromophores [6,8], the experimental ΔH values may be attributed to a rearrangement of atoms in the coordination polyhedra of manganese(II), given by

$$\begin{array}{l} Mn[O_2^*O_4] \searrow \\ \qquad\qquad\qquad Mn[^*O_6] \\ Mn[^*O_2N_4] \nearrow \end{array}$$

The present series of compounds do not give any definite indication of any regularity in the order of the relative Lewis acidity of the divalent manganese salts.

CONCLUSION

From the foregoing discussion, it may be inferred that in the salt hydrates the water molecules are as strongly bound to the metal ion as the pyridine molecules in a routine complex. This unambiguously suggests that salt hydrates are better materials for energy storage application than the pyridine complexes, in spite of the fact that pyridine is a stronger Lewis base.

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