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THE THERMOCHEMISTRY OF THE DECOMPOSITION OF MANGANESE(II) OXALATE DIHYDRATE

MICHAEL EWART BROWN
Chemistry Department, Rhodes University, Grahamstown, 6140 (South Africa)
DAVID DOLLIMORE
Department of Chemistry, University of Salford, Salford M5 4WT (England)
ANDREW K. GALWEY
Department of Chemistry, Queen's University, Belfast BT9 5AG (Northern Ireland)
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ABSTRACT

Differential scanning calorimetry (DSC) has been used to determine the enthalpy of dehydration of manganese(II) oxalate dihydrate and the enthalpies of decomposition in nitrogen and in oxygen of the anhydrous oxalate. The thermodynamic data have been related to the activation energies reported in kinetic studies and to the mechanisms proposed for the thermal decomposition and oxidation processes.

INTRODUCTION

There is a considerable literature devoted to the investigation of reactions which occur on heating manganese(II) oxalate dihydrate (MOD). Kinetic studies have been concerned with both dehydration[1,2] and the subsequent decomposition of the anhydrous oxalate in various atmospheres[3–9]. Recently, detailed reaction mechanisms for the latter reaction in inert and in oxidizing atmospheres (referred to henceforth as the oxidizing reaction) have been proposed[10]. This work included the investigation by electron microscopy of the textural changes which accompanies dehydration, decomposition and oxidation.

An important feature of the dehydration is a characteristic dependence of the rate of water loss upon the prevailing water vapour pressure[1], a pattern of behaviour which has become known as the *Smith-Topley Effect*. The conditions of dehydration influence the structure of the anhydrous oxalate and such variations, in turn, exert some control upon the kinetics of subsequent decomposition or oxidation[10]. Values of the activation energy reported in the literature[2,11] range between 70–100 kJ mol^{-1} for the dehydration, and from 140 to 185 kJ mol^{-1} for decomposition. These variations have been attributed to differences in the defect structure of the anhydrous

TABLE 1

SOME POSSIBLE REACTIONS OF MANGANESE(II) OXALATE

Dehydration

$$MnC_2O_4 \cdot 2H_2O(s) \rightarrow MnC_2O_4(s) + 2H_2O(g) \tag{1}$$

Decomposition

$$MnC_2O_4(s) \rightarrow MnO(s) + CO(g) + CO_2(g) \tag{2}$$

$$MnC_2O_4(s) \rightarrow \frac{1}{3}Mn_3O_4(s) + \frac{4}{3}CO(g) + \frac{2}{3}CO_2(g) \tag{3}$$

$$MnC_2O_4(s) \rightarrow \frac{1}{2}Mn_2O_3(s) + \frac{3}{2}CO(g) + \frac{1}{2}CO_2(g) \tag{4}$$

Oxidation

$$MnO(s) + \frac{1}{4}O_2(g) \rightarrow \frac{1}{2}Mn_2O_3(s) \tag{5}$$

$$MnO(s) + \frac{1}{6}O_2(g) \rightarrow \frac{1}{3}Mn_3O_4(s) \tag{6}$$

$$\frac{1}{3}Mn_3O_4(s) + \frac{1}{12}O_2(g) \rightarrow \frac{1}{2}Mn_2O_3(s) \tag{7}$$

$$MnC_2O_4(s) + \frac{3}{4}O_2(g) \rightarrow \frac{1}{2}Mn_2O_3(s) + 2CO_2 \tag{8}$$

$$MnC_2O_4(s) + O_2(g) \rightarrow MnO_2(s) + 2CO_2 \tag{9}$$

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oxalate as the solid product of the dehydration reaction and reactant for decomposition. The activation energy for the oxidation reaction is 100 kJ mol^{-1} and the value for the decomposition of the oxalate ion in KBr[12, 13] is 250–265 kJ mol^{-1}.

It is predicted from thermodynamic considerations[11] that the solid products of pyrolysis of manganese(II) oxalate are oxides and possible stoichiometric reactions, which may participate in salt decomposition and oxidation, are given in Table 1, each is numbered for reference. Thermodynamic data for the reactants and products listed in Table 1 are given in Table 2. The predicted standard enthalpies of reactions (1) to (9) are listed in Table 3, together with the corresponding calculated percentage mass losses. Although there have been DTA studies of the dehydration, decomposition in nitrogen and oxidation of MOD[4, 5], no estimates of the enthalpies of these processes have been made. The present article reports measured enthalpies of reaction, results are compared with the predictions of Table 3 and considered with reference to both the structure of the anhydrous salt and the composition of the residual oxide.

EXPERIMENTAL

Manganese (II) oxalate dihydrate

The samples of salt used throughout the present work were from the same preparation of reactant as studied previously[3, 10] and were subjected to an identical dehydration procedure where appropriate. The *vacuum-dehydrated* salt (MOV) was evacuated to $\sim 10^{-5}$ Torr, slowly heated ($\sim$ 30 min) to 460K and held for 2 h at this temperature with maintained pumping. The *air-dehydrated* salt (MOA) was held at 460K for 2h, in the atmosphere, then evacuated 1 h, while heating was continued.

X-ray diffraction patterns for MOD and for the anydrous salt were in agreement with published data[14]. As expected[15] the degree of crystallinity, adjudged from X-ray diffraction photographs, was greater for MOA than for MOV. On exposure to water vapour the anhydrous material was completely converted to the dihydrate.

Apparatus

Enthalpies of reaction were measured using a Perkin-Elmer DSC-2 differential scanning calorimeter, calibrated in the usual way, by melting known masses of pure metals. Decomposition reactions in nitrogen were studied using samples in uncrimped gold pans, while for the lower temperature oxidation reactions the usual crimped and pierced aluminium pans were used.

RESULTS AND DISCUSSION

The DSC curve for MOD in nitrogen, heated at 20K min^{-1} (Fig. 1) shows the occurrence of two distinct endothermic processes, identified as dehydration (onset

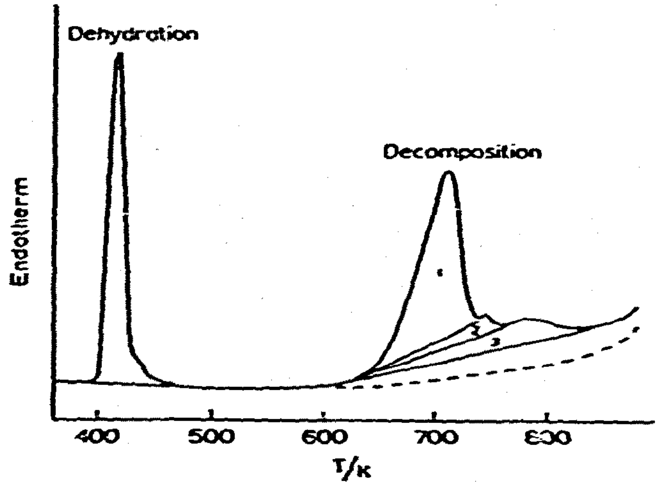

Fig. 1. A representative DSC response trace for the dehydration and decomposition reactions detected on heating (at 20K min^{-1}) a 5.21 mg sample of manganese (II) oxalate dihydrate in nitrogen using a gold sample pan. Water loss and anion breakdown are distinct and separate processes. The latter reaction is complex, the three areas marked are in the ratio 63 : 8 : 29 for 1 : 2 : 3, respectively; the dotted line indicates the baseline trace during sample rerun.

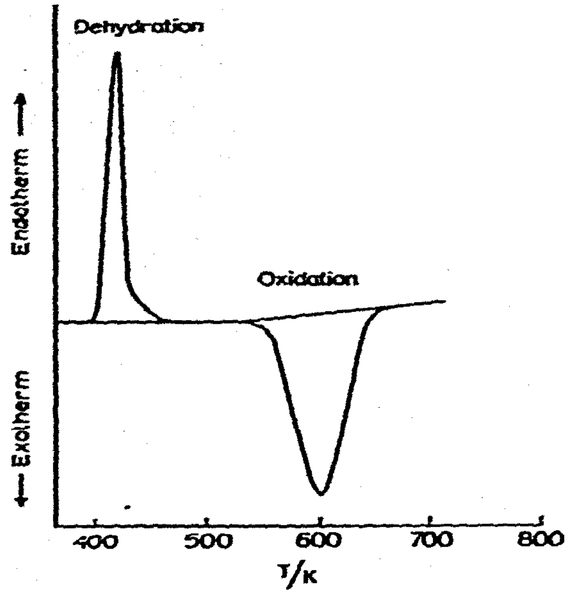

Fig. 2. A representative DSC response trace for the dehydration and oxidation reactions of manganese(II) oxalate on heating (at 20K min^{-1}) a 3.93 mg sample of salt in oxygen. As with the reaction in nitrogen (Fig. 1) water loss and anion breakdown proceed as separate reactions; here, however, the latter step occurs at a somewhat lower temperature, is exothermic and there is no evidence of subsidiary processes.

380K, main peak maximum at 420K, followed by a small shoulder) and decomposition (onset 630K, main peak maximum 715K, followed by at least two further small overlapping responses). Under these conditions the solid product has been identified[5] as MnO of high surface area. No evidence was apparent in the DSC response trace of any sharp recrystallization process between dehydration and decomposition.

DSC curves for vacuum (MOV) and air (MOA) prepared anhydrous oxalate showed that small quantities of water were retained or readsorbed by the dehydrated salt. X-ray powder photographs showed that removal of this residual water did not improve the crystallinity of MOV.

Salt (MOD) heated in oxygen (also at 20K min^{-1}) gave a dehydration endotherm which was essentially identical with that on heating in nitrogen. The subsequent reaction, corresponding to the oxidation process, was exothermic and occurred at a somewhat lower temperature (onset 530K, maximum 605K) (Fig. 2).

DEHYDRATION

The enthalpy of dehydration, both in nitrogen and in oxygen, was determined as 130± 5kJ $(\text{mol MOD})^{-1}$, or, on average, 65± 5kJ $(\text{mol } H_2O)^{-1}$. There was no evidence to suggest that the two water molecules were released through distinct successive steps, though the last traces of water were relatively more difficult to remove. The low observed values for the activation energy of dehydration (70–100kJ mol^{-1})

TABLE 2

LITERATURE VALUES OF STANDARD ENTHALPIES OF FORMATION AT 298K OF REACTANTS AND PRODUCTS OF REACTIONS OF MANGANESE(II) OXALATE DIHYDRATE

All values from ref. 16 except that of $MnC_2O_4(s)$ which was from ref. 17.

	ΔH_f° (kJ mol^{-1})
$MnC_2O_4 \cdot 2H_2O(s)$	−1626
$MnC_2O_4(s)$	−1080
$MnO(s)$	− 385
$Mn_2O_3(s)$	− 959
$Mn_3O_4(s)$	−1388
$MnO_2(s)$	− 520
$CO(g)$	− 110
$CO_2(g)$	− 394
$H_2O(g)$	− 242
$H_2O(l)$	− 285

confirms the suggestion by Smith and Topley[1] that a single water molecule participates in the activated complex for dehydration. It is expected, therefore, that the activation energy for the rehydration reaction is in the range 5 to 35kJ mol^{-1}.

The value of the standard enthalpy of dehydration of MOD calculated from published data (Table 2) is 62kJ (mol MOD)$^{-1}$. The most probable reason for the difference between this value and our measured magnitude is the uncertainty in the value of ΔH_f° for the anhydrous oxalate. Some of this discrepancy could arise from variation of the physical form of the samples compared, there is also the problem of ensuring complete dehydration has been achieved and that no rehydration has occurred. Taking the reported value of ΔH_f° for MOD with our measured enthalpy of dehydration in nitrogen or oxygen, we find that ΔH_f° for the anhydrous oxalate is −1012 kJ mol^{-1} which represents a variation of some ~ 7% from the magnitude listed in Table 2 (−1080kJ mol^{-1}, Le Van and Perinet[17] quote an expected imprecision of $\pm$ 40kJ mol^{-1}).

OXIDATION

The solid product of MOD oxidation was identified as γ-Mn_2O_3 from powder X-ray diffraction measurements, but the production, in small yields, of other oxides cannot be excluded. Dollimore et al.[11] found that the course of thermal decomposition in air depended on the heating rate. When the temperature increase was rapid, as in the initial period of heating prior to an isothermal experiment, reaction yielded γ-Mn_2O_3 or Mn_3O_4 whereas production of the more stable structure α-Mn_2O_3 was favoured during thermal analysis at a slow heating rate. The conversion of Mn_2O_3 to Mn_3O_4 occurs[18] only above 1220K which is above the range of the DSC-2.

TABLE 3

ENTHALPIES OF REACTIONS LISTED IN TABLE 1 CALCULATED FROM LITERATURE DATA GIVEN IN TABLE 2

Reaction	*Type*	*Solid product*	*ΔH°(kJ(mol $MnC_2O_4 \cdot 2H_2O$)$^{-1}$)*	*Mass loss (based on dihydrate)*
(1)	Dehyd.	MnC_2O_4	61.9	20.11
(2)	Decomp.	MnO	191	60.3
(3)	Decomp.	Mn_3O_4	208	57.4
(4)	Decomp.	Mn_2O_3	239	55.9
(5)		Mn_2O_3	−94.5	
(6)		Mn_3O_4	−77.7	
(7)		Mn_2O_3	−16.8	
(8)	Oxid.	Mn_2O_3	−188	55.9
(9)	Oxid.	MnO_2	−228	51.4

The enthalpy of the oxidation reaction was determined, from the single peak (Fig. 2), as −300±10kJ (mol MOD)$^{-1}$ compared with the predicted value of −188kJ (mol MOD)$^{-1}$ (see Table 3) for reaction (8) yielding Mn_2O_3(s). This lack of agreement is improved if the lower value (see above) of −1012 (mol MOD)$^{-1}$ is used for ΔH_f° of the anhydrous oxalate: on this basis the expected ΔH_f° for reaction (8) is −256kJ (mol MOD)$^{-1}$. It is also possible that contributions to the overall enthalpy change may result from non-stoichiometry of the residual oxide or the production of minor amounts of phases other than Mn_2O_3. Moreover, no information is available concerning the enthalpy of the transition

γ-$Mn_2O_3(s) \rightarrow \alpha$-$Mn_2O_3(s)$.

DECOMPOSITION

Determination of the enthalpy of decomposition of manganese(II) oxalate in nitrogen is complicated by the occurrence of successive overlapping endotherms and uncertainties in the baseline. Attempts to eliminate the latter contribution to error were made by a second heating of the decomposed material under the same conditions and are indicated as the dotted line in Fig. 1. Specific procedures for the establishment of the baseline[19, 20] were not applied here since it is obvious that the reactions occurring are complex.

The enthalpy of decomposition of anhydrous manganese(II) oxalate, as determined from the total endothermic response (i.e., area 1+2+3) in Fig. 1, was 250±25kJ (mol MOD). Values obtained for the same reaction of two different preparations of the anhydrous oxalate, MOV and MOA, did not vary beyond these error limits. At lower heating rates the region marked 3 was less distinct so that the baseline bounded regions 1+2 only, with a reduction of some 29% in the response

TABLE 4

EXPERIMENTALLY MEASURED DATA FOR REACTIONS OF MANGANESE(II) OXALATE DIHYDRATE: ENTHALPIES (FROM DSC DATA) AND WEIGHT LOSS

	ΔH(kJ(mol MOD)$^{-1}$)	*Percentage mass-loss (ref. to MOD)*
Dehydration	130 ± 5	19.5 ± 0.2
Decomposition	250 ± 25	58.5 ± 0.5
Oxidation	−300 ± 10	52.0 ± 0.5

area or an enthalpy value of 178kJ (mol MOD)$^{-1}$. Area 1 (only) corresponded to an enthalpy of 158kJ (mol MOD)$^{-1}$.

The standard enthalpy of decomposition of the anhydrous oxalate, predicted for reaction(2) of Table 1, using the data in Table 2, is 191kJ (mol MOD)$^{-1}$. Using the lower value of the enthalpy of formation of anhydrous oxalate from the dehydration measurements reported above, the enthalpy of decomposition is reduced to 123kJ (mol MOD)$^{-1}$.

While peak area 1 corresponds approximately with thermodynamic expectation for the decomposition reaction, it is clear that the overall process is not quantitatively represented by eqn (2) Table 1. Thermochemical measurements indicate the occurrence of three contributory steps in the overall change and evolved gas analyses[10] show progressive variation in the [CO]/[CO_2] ratio during the course of the reaction. Previously[10] we have attributed the evolution of a small excess of carbon dioxide to some reduction of MnO; the thermochemical consequences of such deviation from stoichiometry cannot be assessed, however, since the necessary enthalpic measurements are not available. The considerable reactivity of the residual manganous oxide product, which is pyrophoric, makes its characterization difficult. The measured mass-loss, 58.5 ± 0.5% (Table 4) provides experimental support for the formation of some reduced oxide.

The suggestion referred to in the previous paragraph, that there is some reduction of the MnO, is based on the observation that the CO_2/CO product ratio for the overall reaction is greater than unity. There is, however, the alternative possibility that not all the carbon is volatilized as oxides and some oxygen is incorporated into the residue. High temperature (1500K) studies[21, 22] of the oxidation–reduction kinetics of single crystals of MnO in CO + CO_2 atmospheres have shown that excess oxygen (up to 2%) may be incorporated in manganese(II) oxide. Although these studies refer to temperatures very much higher than those required to decompose MOD, the finely divided product of the pyrolysis reaction is expected to be very much more reactive than the large single crystals of the oxidation–reduction work.

It has been proposed[10] that Mn^{3+} is an intermediate in the decomposition of anhydrous manganese(II) oxalate. Any occurrence of the reaction

$$MnO\,(s) + \tfrac{1}{2}\,CO_2\,(g) \rightarrow \tfrac{1}{2}\,Mn_2O_3(s) + \tfrac{1}{2}\,CO\,(g)$$

which has an enthalpy of 48kJ, would add to the endothermic nature of decomposition.

Thus we conclude that this thermochemical evidence supports the earlier observations[10] that the residue from decomposition of manganese(II) oxalate in nitrogen is non-stoichiometric, but the constituent in excess or in deficit is not identified. The overall change is not quantitatively represented by eqn (2) of Table I.

The wide range of enthalpy values, 123kJ (mol MOD)$^{-1}$ estimated for reaction (2) to the measured value (250 ± 25 kJ (mol MOD)$^{-1}$), when compared with the range of reported activation energies (140 to 265 kJ mol^{-1}), still allows for one oxalate ion in the activated complex or decomposition configuration, subject to the reservations expressed by Garn[23]. Boldyrev et al.[24] have identified the activation energy for decomposition with the energy required to break the C–C bond in the oxalate ion.

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