Note

Thermal decomposition of manganese(II) dicarboxylate anhydrides in various atmospheres

Yukihiko Suzuki [a,*], Kazuo Muraishi [b], Hiroko Ito [c]

[a] *Department of Applied Chemistry, Faculty of Engineering, Yamagata University, Jonan,*
4-3-16 Yonezawa 992, Japan
[b] *Yamagata Women's Junior College, Katayaji Yamagata, 990-23, Japan*
[c] *NEC Ltd. Co., Yamagata Manufacture, 990, Japan*

Abstract

The thermal decomposition of Mn(II) dicarboxylate anhydride $Mn[OOC(CH_2)_nCOO]$ ($n = 0$, 1–8) was studied using simultaneous non-isothermal techniques (TG and DTA). It was shown that CO_2 has an inhibiting effect on the decomposition whereas air has an accelerating effect, both relative to Ar. The final products are MnO in Ar and CO_2, and Mn_3O_4 in air, as characterized by chemical analysis, IR spectroscopy and XRD measurements. In general the initial decomposition temperatures in Ar were found to decrease with increasing number of CH_2 groups.

Keywords: Dicarboxylate anhydride; Manganese(II) dicarboxylate; Metal dicarboxylate; Thermal decomposition; Various atmospheres

1. Introduction

The effects on the thermal decomposition reactions of manganese(II) dicarboxylate anhydride of systematically varying the cation and keeping the same carboxylate anion have been extensively investigated using TG and DTA.

Recently, the literature has contained a remarkable amount of data on the thermal dehydration and decomposition of various oxalates, malonates and succinates:

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* Corresponding author.

$Li_2C_2O_4$ [1], $CaC_2O_4 \cdot H_2O$ [2], $MC_2O_4 \cdot H_2O$ (M is Ca, Sr, Ba) [3], $CrC_2O_4 \cdot 2H_2O$ [4], $MC_2O_4 \cdot 2H_2O$ (M is Co, Ni) [5], $An_2 (C_2O_4) \cdot nH_2O$ (An is Am, Cm, Bk, Cf) [6], $Co[Co(C_2O_4)_2] \cdot 4H_2O$ [7], $Mn[Mn(C_2O_4)_2] \cdot 4H_2O$ [8], $M_2C_3H_2O_4 \cdot XH_2O$ (M is Na, K, Rb, Cs; $X = 1, 1, 5, 6$) [9a], $M_2C_3H_2O_4$ (M is Li, Na, k, Rb, Cs) [9b], $M_2C_3H_2O_4$ (M is Li, Na, k, NH$_4$) [10], $MgC_3H_2O_4 \cdot 3H_2O$ [11], $CaC_3H_2O_4 \cdot 2H_2O$ [12], $NiC_3H_2O_4$ [13], $MC_3H_2O_4 \cdot XH_2O$ (M is Co, Ni, Cu, Zn; $X = 2, 1, 2.5, 2$) [14], $Mg_3[Fe(C_3H_2O_4)_3] \cdot 10H_2O$ [15]; alkali metal succinates [16], $MC_4H_4O_4 \cdot XH_2O$ (M is Co, Ni, Cu, Zn; $X = 2, 2, 0.5, 0.5$) [17], $MC_4H_4O_4$ (M is Fe, Co, Ni, Cu) [18].

However, except for the thermal decompositions of silver dicarboxylates with even numbered CH_2 groups [19] and yttrium dicarboxylates [20], there is little or no information in the literature on the thermal decomposition of series of metal dicarboxylates with the same cation and varying the dicarboxylate anion.

Burleva and his co-workers [19] have found that the thermal decomposition of Ag dicarboxylates with an even number of CH_2 groups gave metallic Ag, CO_2 and organic diradicals as primary products, and polymers as secondary products in vacuo. They found that Ag dicarboxylates with higher numbers of CH_2 groups were much more stable to thermal treatment than Ag oxalate. A thermochemical investigation of the dehydration and decomposition of Y dicarboxylate hydrates was reported by Brzyska and Ożga [20]. On heating, Y malonate, succinate, glutarate, azelate and sebacate lose crystallization water and the anhydrous compounds are transformed to Y_2O_3; whereas Y adipate, pimelate and suberate on heating lose some water molecules and the mono- or dihydrates formed are decomposed to Y_2O_3. Furthermore, it has been found that the activation energies of the dehydration change discretely in the dicarboxylate series, as well as the temperatures of the decomposition and Y_2O_3 formation. The extraordinary versatility of dicarboxylic ligands upon coordination is well known and this, together with the many polymeric species present, effects their structural chemistry.

Mn(II) compounds are labile and their ionic radii are larger than for other low first transition metals. Many Mn(II) dicarboxylates $(Mn(COO)_2(CH_2)_n, n = 0, 1–8)$ are unstable when they are heated in air. This sensitivity to oxygen and the products of the reactions are a major reason for the increasing interest in manganese chemistry. Furthermore, it is indicated that the decomposition processes of Mn(II) dicarboxylates are very complicated mainly due to the variable valence of manganese. The numbers of possible oxides and the conditions under which they form in the decomposition products are responsible for the complexity of the TG and DTA patterns.

This paper describes a study of the thermal decomposition of anhydrous Mn(II) dicarboxylates to determine the formation temperatures of several oxides, and to obtain information about the decomposition products.

2. Experimental

2.1. Materials

The Mn(II) dicarboxylates used and their preparation and thermal dehydration have been described in a previous paper [21]. The crystals obtained were dried by gentle

pressure between filter papers, and then stored in a desiccator over P_2O_5 and silica gel for several days.

2.2. Measurements

All the TG–DTA curves were obtained with a Shinku Riko TGD-3000 apparatus using flowing Ar, CO_2 or air atmospheres at 200 ml min^{-1} and a heating rate of 10°C min^{-1}. About 30 mg of powdered sample in a platinum crucible was used for each run. The IR spectra in the frequency region of 4000–650 cm^{-1} were obtained by the KBr disc method with a Hitachi 215 IR spectrophotometer. The powder X-ray diffraction analysis was made with a Rigaku Denki DS X-ray diffractometer. Other experimental details were similar to those described previously [22].

3. Results and discussion

The TG–DTA curves of Mn(II) dicarboxylate anhydrides which include the thermal dehydration process from room temperature to 1000°C in flowing atmospheres of air and Ar are shown in Figs. 1 and 2. Table 1 summarizes the initial decomposition temperatures (T_i), the DTA peak temperatures (T_m), the weight-loss values (ΔW) and the products in the final step. Table 1 does not include data for the thermal dehydration process described in Ref. [21]. The products were determined by appropriate combinations of TG, X-ray diffraction analysis, evolved gas analysis and combustion analysis for elemental carbon. The decomposition in CO_2 was similar to that in Ar. The features of the thermal decomposition on the TG–DTA curves in Ar, CO_2 and air atmospheres have a tendency to become complicated with increasing numbers of CH_2 groups in the dicarboxylates. The decomposition pathways in Ar of oxalate–pimelate ($n = 0$, 1–5) proceed in two stages, whereas those of suberate–sebacate ($n = 6$–8) take place in three or more steps.

The thermal decomposition in CO_2 takes place at a higher temperature and proceeds more sluggishly compared with that in Ar and in an oxidizing atmosphere such as air (Table 1). As expected from the rule of chemical equilibrium, the decomposition reactions are depressed in CO_2, because the main gaseous product was found to be CO_2.

In air, the reaction proceeds rapidly above about 270–310°C. A sharp exothermic peak occurs due to oxidation of the organic portion. The IR and XRD spectra of Mn(II) glutarate, adipate, pimelate and suberate heat-treated at different temperatures in air are shown in Figs. 3 and 4. The IR bands due to dicarboxylate ion disappear on heating at 330–350°C.

Essentially, similar data were obtained with the other Mn(II) dicarboxylates. Mn(II) glutarate, adipate, pimelate and suberate heated at 330, 330, 350 and 290°C in air were amorphous to X-rays (Fig. 4). On further heating, the product obtained is α-Mn_2O_3, the oxide stable from about 550 to 940°C. The solid product formed in air is Mn_2O_3 (JCPDS Card 24-0508); no elementary carbon was formed in this atmosphere, because the following reactions are thermodynamically possible at the decomposition tempera-
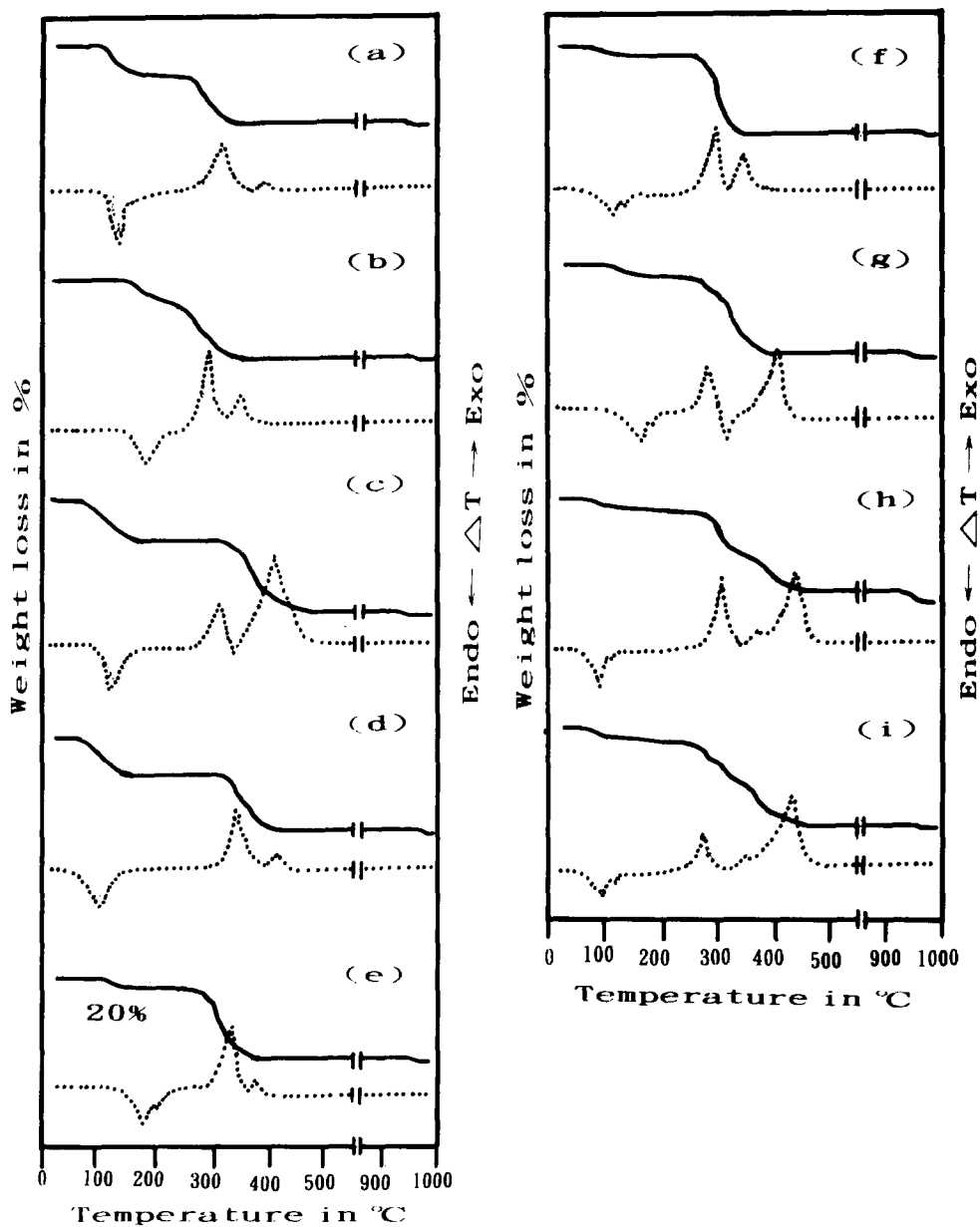
Fig. 1. TG (solid line) and DTA (dotted line) curves of Mn(II) dicarboxylate hydrates in air atmosphere: heating rate, 10°C min^{-1}; flow rate, 200 ml min^{-1}. (a) Oxalate; (b) malonate; (c) succinate; (d) glutarate; (e) adipate; (f) pimelate; (g) suberate; (h) azelate; (i) sebacate.

Fig. 2. TG (solid line) and DTA (dotted line) curves of Mn(II) dicarboxylate hydrates in Ar atmosphere: heating rate, 10°C min⁻¹; flow rate 200 ml min⁻¹. (a) Oxalate; (b) malonate; (c) succinate; (d) glutarate; (e) adipate; (f) pimelate; (g) suberate; (h) azelate; (i) sebacate.
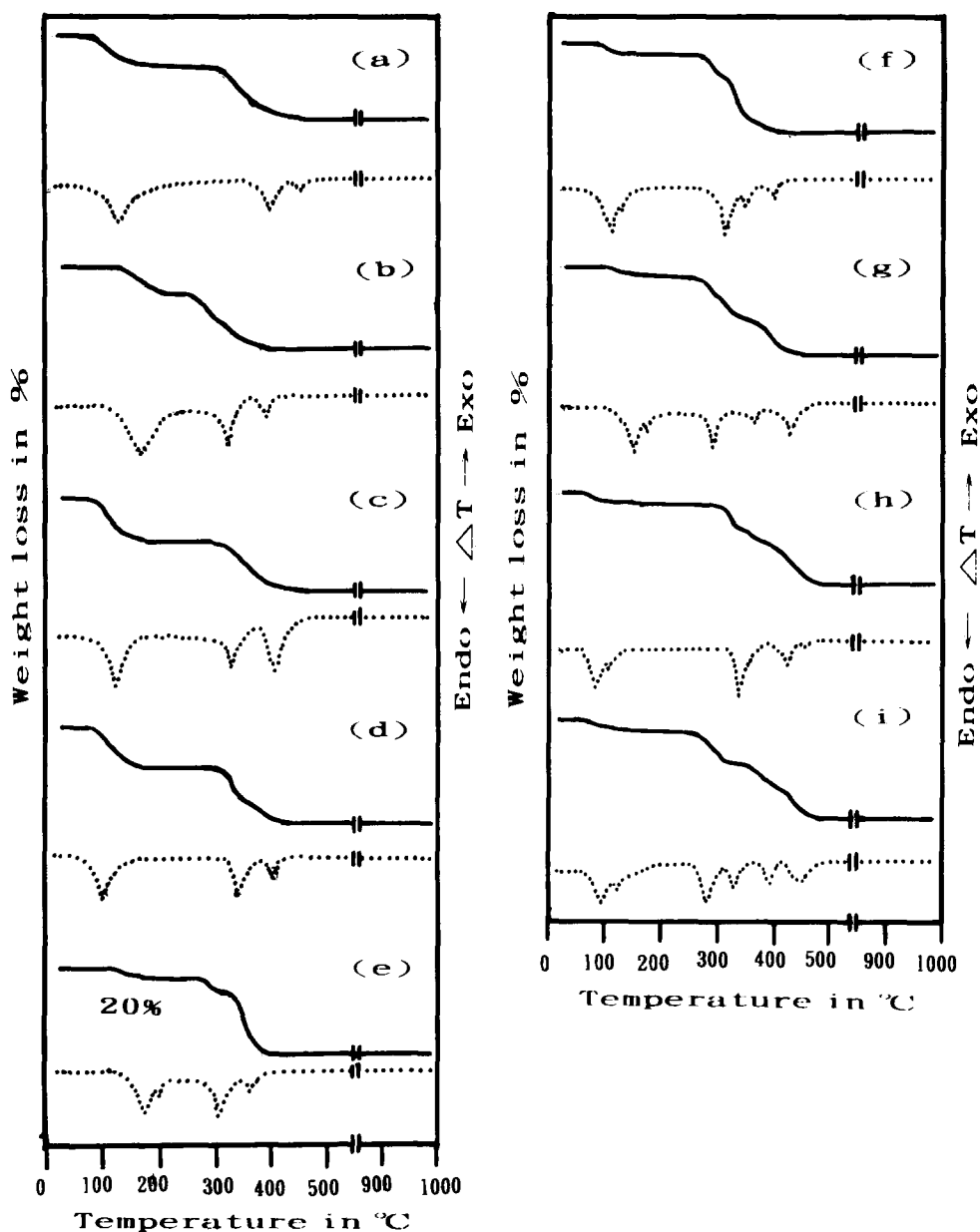
Table 1
Thermal decomposition data of Mn(II) dicarboxylate anhydrides in various atmospheres: T_i, initial decomposition temperatures; T_m, DTA peak temperatures; ΔW, weight-loss values

Compound	Atmosphere	$T_i/^\circ C$	$T_m/^\circ C$	ΔW obsd/%	ΔW calcd/%	Product
MnC_2O_4	Ar	324	400	36.23	38.00	$MnO + 0.5C$
	CO_2	343	421	36.19	38.00	$MnO + 0.5C$
	Air	274	318	34.18	34.09	$Mn_2O_3 + 0.5C$
		963	–	37.24	37.26	Mn_3O_4
$MnC_3H_2O_4$	Ar	286	315	38.27	38.35	$MnO + C$
	CO_2	302	327	39.23	38.35	$MnO + C$
	Air	268	280	37.02	37.32	$Mn_2O_3 + C$
		961	–	41.79	41.82	Mn_3O_4
$MnC_4H_4O_4$	Ar	314	318	36.12	36.24	$MnO + C$
	CO_2	320	325	36.09	36.24	$MnO + C$
	Air	297	308	35.40	35.42	$Mn_2O_3 + C$
		944	–	38.75	38.98	Mn_3O_4
$MnC_5H_6O_4$	Ar	313	333	38.60	39.71	$MnO + C$
	CO_2	322	333	38.67	39.71	$MnO + C$
	Air	310	337	38.73	38.93	$Mn_2O_3 + C$
		970	–	42.28	42.31	Mn_3O_4
$MnC_6H_8O_4$	Ar	293	310	50.81	50.72	$MnO + 1.5C$
	CO_2	299	308	49.27	50.72	$MnO + 1.5C$
	Air	290	305	50.12	51.19	$Mn_2O_3 + 1.5C$
		950	–	56.24	56.57	Mn_3O_4
$MnC_7H_{10}O_4$	Ar	294	306	53.68	53.72	$MnO + 1.5C$
	CO_2	300	307	53.52	53.72	$MnO + 1.5C$
	Air	288	300	53.95	54.16	$Mn_2O_3 + 1.5C$
		960	–	59.13	59.21	Mn_3O_4
$MnC_8H_{12}O_4$	Ar	288	295	55.49	56.36	$MnO + 1.5C$
	CO_2	287	298	55.42	56.36	$MnO + 1.5C$
	Air	280	292	56.55	56.77	$Mn_2O_3 + 1.5C$
		941	–	60.73	61.54	Mn_3O_4
$MnC_9H_{14}O_4$	Ar	305	327	55.98	56.41	$MnO + 2C$
	CO_2	309	325	55.37	56.41	$MnO + 2C$
	Air	295	300	57.62	57.96	$Mn_2O_3 + 2C$
		954	–	63.15	63.62	Mn_3O_4
$MnC_{10}H_{16}O_4$	Ar	274	282	58.53	58.65	$MnO + 2C$
	CO_2	275	285	59.27	58.65	$MnO + 2C$
	Air	273	278	59.96	60.12	$Mn_2O_3 + 2C$
		950	–	65.51	65.49	Mn_3O_4

tures of the dicarboxylates

$$2MnO + 0.5O_2 \rightarrow Mn_2O_3 \tag{1}$$

$$C + O_2 \rightarrow CO_2 \tag{2}$$

Although disagreement continues as to whether Mn_2O_3 should be formulated as $Mn^{II}Mn_2^{III}O_4$ or $Mn^{IV}Mn_2^{II}O_4$, neutron diffraction data suggest that $Mn^{II}Mn_2^{III}O_4$ is
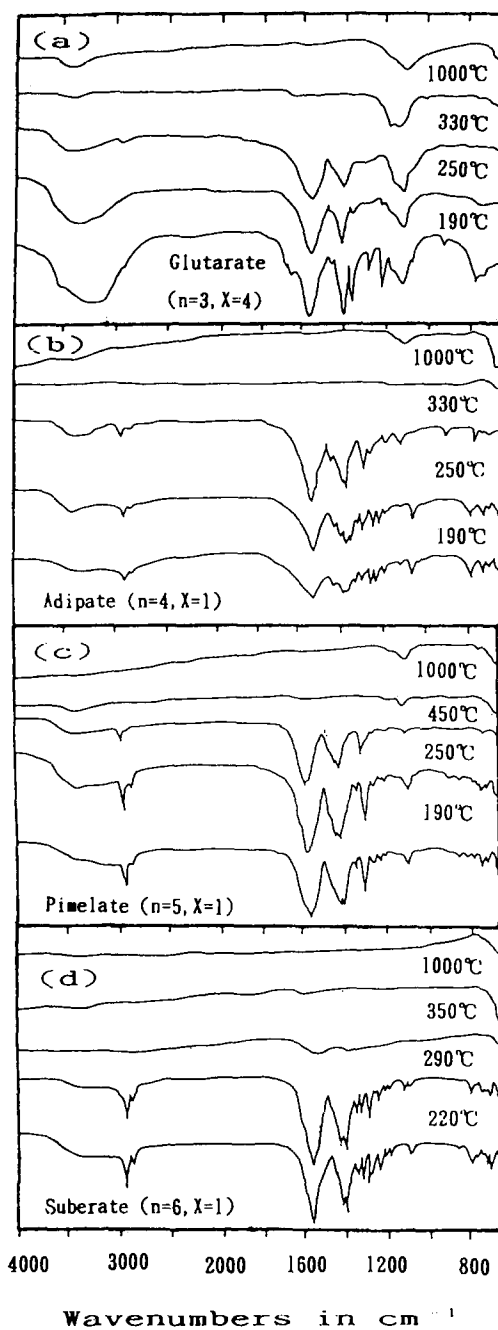
Fig. 3. IR spectra of typical Mn(II) dicarboxylate hydrates heated at different temperatures in air.
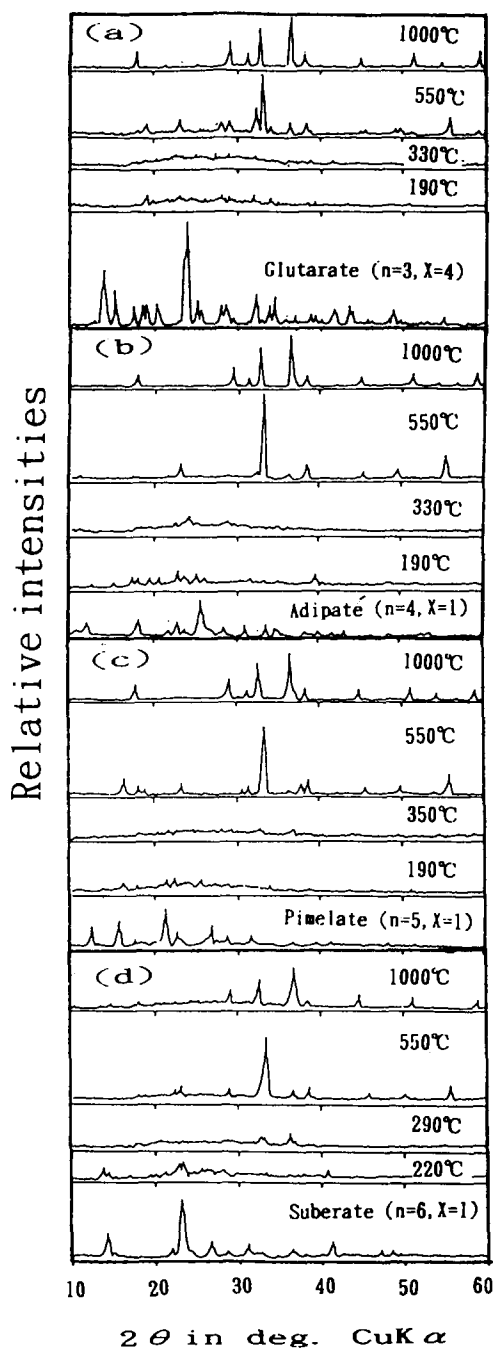
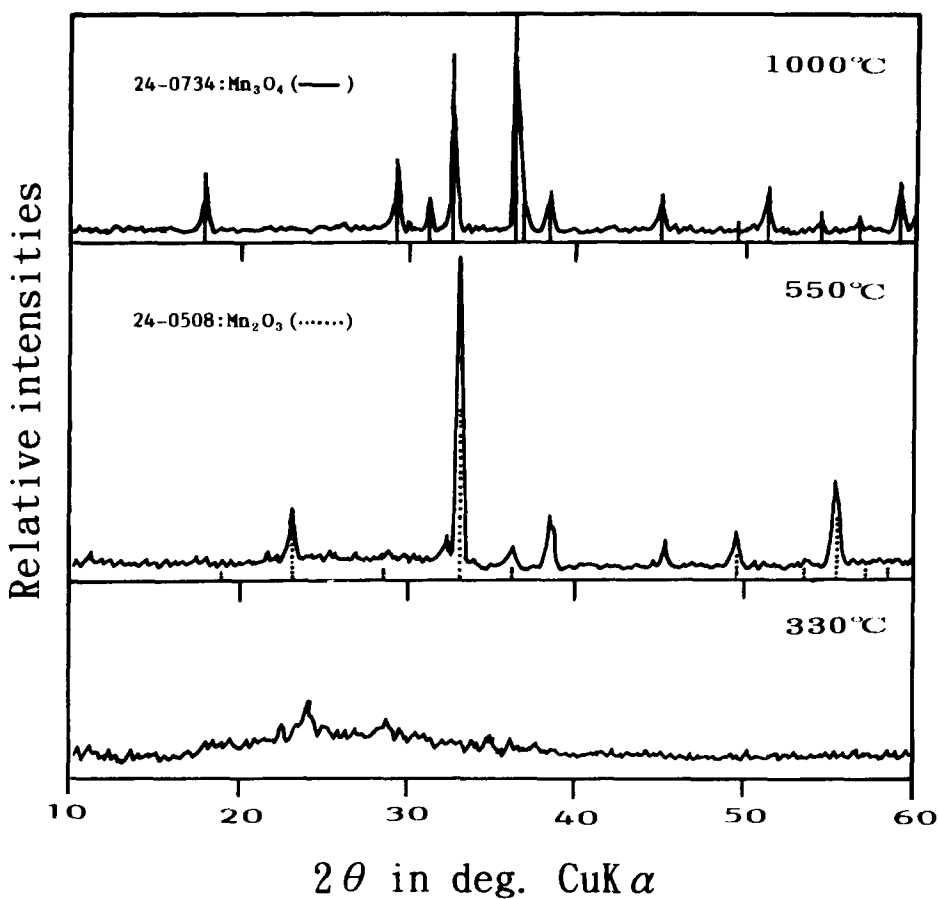Fig. 4. XRD patterns of typical Mn(II) dicarboxylate hydrates heated at different temperatures in air.

Fig. 5. Relation between XRD patterns of Mn oxides obtained by heating Mn(II) adipate at different temperatures in air and JCPDS Cards of Mn_2O_3 and Mn_3O_4.

the correct structure [23]. The weight loss at about 940–970°C is attributed to the decomposition of Mn_2O_3 to Mn_3O_4 (JCPDS Card 24-0734), which is consistent with XRD results (Fig. 4 and as adipate of Fig. 5).

In Ar and CO_2 atmospheres, the major product is MnO with the same amount of carbon. The amount of carbon seems to depend somewhat on the ΔG_f of MnO [24] and on the reaction scheme, although further investigations of many other metals are required to clarify these dependences. The disproportionation of CO_2 represented by reaction (3) is thermodynamically favorable.

$$2CO \rightarrow CO_2 + C \tag{3}$$
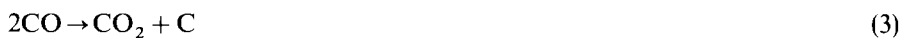
It may be suggested that most of the C and CO_2 formed were produced directly from the decomposition of the dicarboxylates. In general, the initial decomposition temperatures (T_i) in Ar tend to decrease with increasing number of
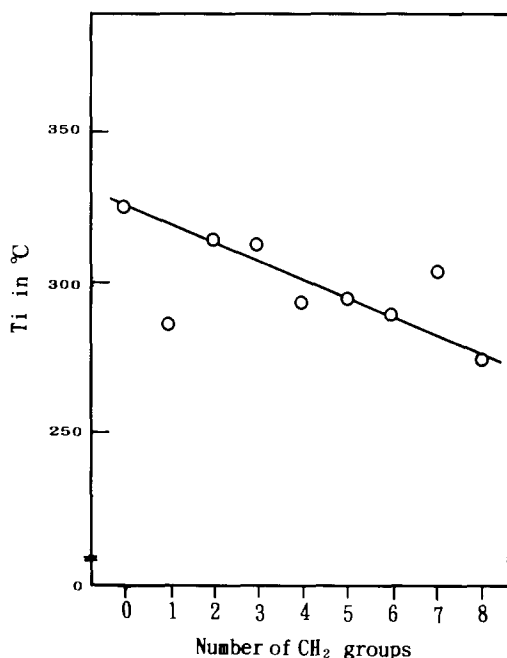
Fig. 6. Relation between initial decomposition temperatures (T_i) in Ar and the number of CH_2 groups in Mn(II) dicarboxylate hydrates.

CH_2 groups in the dicarboxylates (Fig. 6). This tendency may occur owing to the bulky dicarboxylate ions with their increasing number of CH_2 groups in the Mn(II) dicarboxylates.

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