Thermochimica Acta, 23 (1978) 125–133
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THERMAL DECOMPOSITION OF BIVALENT TRANSITION METAL MALONATES IN VARIOUS ATMOSPHERES

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(Received 19 April 1977)

ABSTRACT

The thermal decomposition of the malonates of bivalent transition metals (Mn, Fe, Co, Ni, Cu and Zn) was investigated by mainly TG–DTA, X-ray diffraction analysis and evolved gas analysis in atmospheres of N_2, CO_2 and O_2 and in the air. It was shown that CO_2 has an inhibiting effect on the decomposition whereas O_2 and air have the accelerating effects on the basis of N_2. The decomposition of the salts investigated can be classified into three groups from solid decomposition products: Mn and Zn malonates gave the metal oxides including 1–1.5 moles of elementary carbon, while Cu and Ni malonates gave the metals with 1–1.5 moles of the carbon. Fe and Co malonates in the last group gave once the metal oxides with 1–0.5 moles of the carbon and the oxides produced were subsequently reduced to the metals by the carbon. A possible reaction mechanism for the malonates was discussed and compared with those of the corresponding oxalates and succinates.

INTRODUCTION

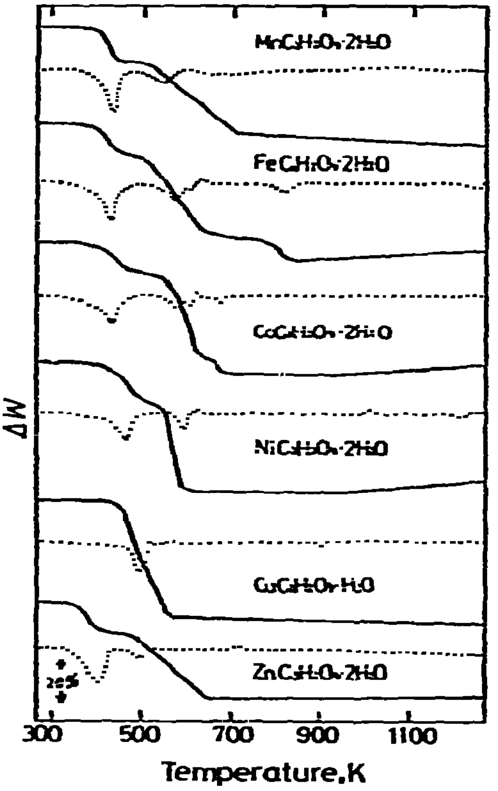
Although many investigations have been carried out on the thermal decomposition of metal dicarboxylates, particularly, of metal oxalates, no systematic attempt has been made on the thermal decomposition of metal malonates. In continuation of our previous study[1] on the thermal dehydration of bivalent transition metal malonate dihydrates, this paper deals with the influence of a systematic change of metal ions and that of ambient atmospheres on the thermal decomposition of the anhydrous salts.

EXPERIMENTAL

The preparations and elemental analysis of the metal malonate dihydrates[1] and the procedures of TG-DTA[1], evolved gas analysis and X-ray powder diffraction analysis[2] were described in preceding papers.

RESULTS

The TG and DTA curves of the malonates over the room temperature to 1300 K in atmospheres of nitrogen, carbon dioxide and oxygen and in the air are shown in Figs. 1–4. The solid lines denote TG curves and the broken lines denote DTA curves. Table 1 summarizes the number of decomposition stage (n), the initial temperature of decomposition (T_i), the peak temperature of DTA (T_m), the weight-loss (ΔW) and the products at each decomposition step. The products were determined



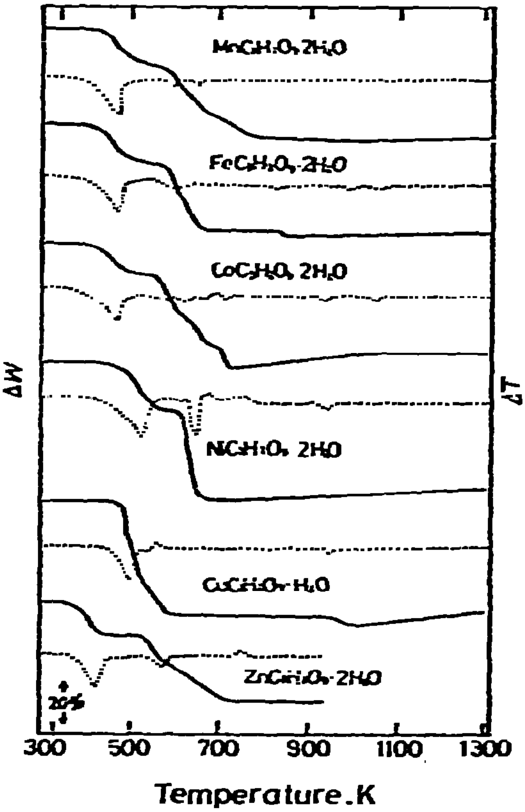
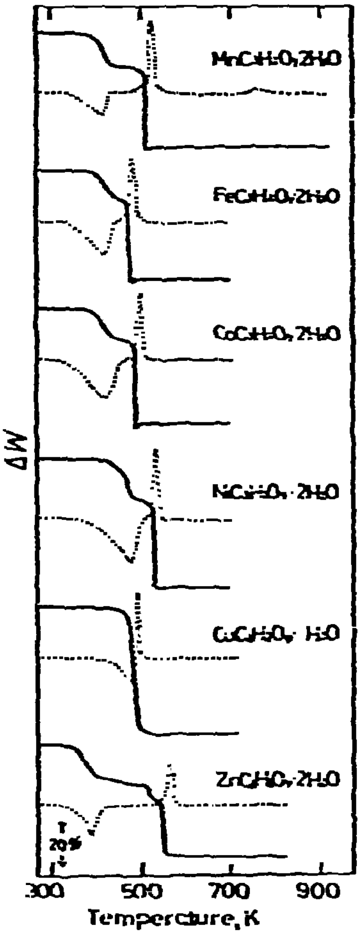


Fig. 1. TG-DTA curves of transition metal malonate hydrates in a flowing nitrogen atmosphere. —, TG; and . . . ., DTA.

Fig. 2. TG-DTA curves of transition metal malonate hydrates in a flowing carbon dioxide atmosphere. —, TG; and . . . ., DTA.



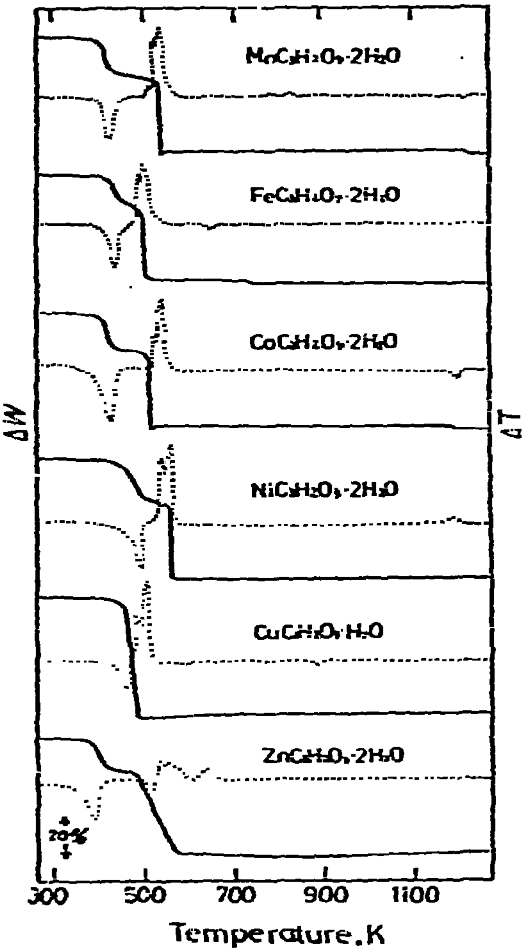


Fig. 3. TG-DTA curves of transition metal malonate hydrates in a flowing oxygen atmosphere. —, TG; and . . . ., DTA.

Fig. 4. TG-DTA curves of transition metal malonate hydrates in a static air atmosphere. —, TG; and . . . ., DTA.

by appropriate combinations of TG, X-ray diffraction analysis, evolved gas analysis and combustion analysis for elementary carbon.

The solid products obtained indicated certain characteristics of the decomposition reactions, which can be summarized as follows: (i) Mn malonate released first about 1/3 moles of CO_2 per mole of the salt and was then decomposed to a mixture of equivalent moles of MnO and elementary carbon in nitrogen and in carbon dioxide, whereas it decomposed directly to Mn_2O_3 in oxygen or in the air except for the preliminary stage with a small weight loss (1–2%). (ii) Fe malonate showed two stages of decomposition corresponding to the formations (FeO + C) and (Fe + 1/2 C), respectively, in nitrogen but the latter stage did not occur in carbon dioxide. In oxygen or in the air, it decomposed directly to Fe_2O_3. (iii) Co malonate decomposed

TABLE 1

THERMAL ANALYSIS DATA OF ANHYDROUS METAL MALONATES IN VARIOUS ATMOSPHERES

Malonate	*Atmosphere*	*n*	$T_i(K)$	$T_m(K)$	ΔW_{obsd} (%)	ΔW_{calcd} (%)	*Product*
$MnC_3H_2O_4$	N_2	2	518	548	8.2	7.6	$- 1/3\ CO_2$
					38.2	38.4	$MnO + C$
	CO_2	2	529	590	8.4	7.6	$- 1/3\ CO_2$
				640	38.6	38.4	$MnO + C$
	O_2	2	493	507	1.4		
				533	41.1	40.4	Mn_2O_3
	Air	2	506	521	2.1		
				536	40.5	40.4	Mn_2O_3
$FeC_3H_2O_4$	N_2	2	503	581	38.3	38.2	$FeO + C$
			675	785	10.7	11.3	$Fe + 1/2\ C$
	CO_2	2	510	590	36.4	38.2	$FeO + C$
				868	2.4		
	O_2	1	475	485	39.6	40.2	Fe_2O_3
	Air	2	483	490	31.2		
				513	37.8	40.2	Fe_2O_3
$CoC_3H_2O_4$	N_2	2	514	607	41.8	40.6	$CoO + 1/2\ C$
				676	8.7	9.1	$Co + 1/3\ C$
	CO_2	2	521	640	36.7	37.6	$CoO + C$
				668	10.7	11.2	$Co + 1/2\ C$
	O_2	1	495	503	41.7	39.6	Co_2O_3
	Air	1	500	525	40.5	39.6	Co_2O_3
$NiC_3H_2O_4$	N_2	1	518	590	46.2	45.7	$Ni + C$
	CO_2	1	527	628	46.5	45.7	$Ni + C$
	O_2	1	486	538	46.6	43.7	NiO
	Air	1	512	540	40.0	43.7	NiO
$CuC_3H_2O_4$	N_2	3	494		11.5		
				502	14.8		
				543	49.1	48.8	$Cu + 1/2\ C$
	CO_2	3	500		9.0		
				505	14.0		
				539	46.5	48.8	$Cu + 1/2\ C$
	O_2	1	491	498	49.3	46.9	CuO
	Air	1	487	500	49.4	46.9	CuO
$ZnC_3H_2O_4$	N_2	2	484	516	9.3	10.8	$- 1/2\ CO_2$
				575	32.1	33.5	$ZnO + 1.5\ C$
	CO_2	2	490	517	8.8	7.2	$- 1/3\ CO_2$
				583	33.2	33.5	$ZnO + 1.5\ C$
	O_2	2	477	515	8.2	7.2	$- 1/3\ CO_2$
				563	40.2	42.3	ZnO
	Air	2	478	513	27.7		
				558	40.7	42.3	ZnO

TABLE 2

THE RATIO OF CO_2/CO EVOLVED AT THE COMPLETE DECOMPOSITION OF THE ANHYDROUS METAL MALONATES IN HELIUM

Metal	*Mn*	*Fe*	*Co*	*Ni*	*Cu*	*Zn*
CO_2/CO	11	0.2	2	8.3	36	16

through the stages of (CoO + 1/2 C) and (Co + 1/3 C) in nitrogen. The decomposition manner in carbon dioxide was similar to that in nitrogen except that a considerable weight increase occurred above 690 K. It decomposed directly to Co_2O_3 in oxygen and in the air. (iv) Ni malonate decomposed in one step to (Ni + C) in nitrogen and in carbon dioxide, and it was also found that an increase in weight occurred in the latter atmosphere above 700 K. The product in oxygen and in the air was NiO. (v) Cu malonate decomposed in one step to (Cu + 1/2 C) in nitrogen and in carbon dioxide, whereas it decomposed to CuO in oxygen and in the air. (vi) Zn malonate released first 1/2–1/3 CO_2 and then decomposed to ZnO in all the atmospheres although 1.5 moles of carbon were included under the decomposition in nitrogen and in carbon dioxide.

The gaseous decomposition products were determined by gas chromatography. CO_2 predominated in the total gaseous products for all the salts except for Co malonate which evolved predominantly CO. The ratios of CO_2/CO given in Table 2 varied with the metals, and the ratios for Mn, Ni, Cu and Zn malonates were much greater than those for the corresponding oxalates, of which the values were about unity[3]. The evolved gases contained H_2, O_2, CH_4, H_2O, $HCOOCH_3$ and $HCOOC_2H_5$ in small portions and the ratios of these gases also varied with the metals, i.e., Mn and Zn malonates giving the metal oxides as a solid product were likely to evolve hydrogen-rich substances such as H_2 and CH_4, whereas Ni and Cu malonates giving the metals evolved O_2 and H_2O in abundance.

Although methyl acetate has been described on the decomposition of Ni malonate by Galwey et al.[4], we found methyl formate instead. At the decomposition temperatures of the salts, however, organic substances with a high molecular weight would be decomposed to CO_2, CH_4, H_2O etc. due to the catalytic action of a nascent metal or metal oxide residue, which may lead to difficulty in their detection.

DISCUSSION

Effects of ambient atmosphere on decomposition products

It is considered to be reasonable that the solid product formed in oxygen or in the air was MO or M_2O_3 and that no elementary carbon was formed in these atmospheres, because the following three reactions are thermodynamically possible at the decomposition temperatures of the malonates.

$$M + 1/2\ O_2 \rightarrow MO \qquad (M = Ni, Cu, Zn)$$
$$2\ MO + 1/2\ O_2 \rightarrow M_2O_3 \qquad (M = Mn, Fe, Co)$$
$$C + O_2 \rightarrow CO_2$$

In the absence of oxygen or at very low partial pressure of oxygen, whether the solid product is M or MO may depend on ΔG values of Reactions (1) and (2) and partial pressures of CO and CO_2, because partial pressures of the other gases were found to be very low from the gas chromatography.

$$M + CO_2 = MO + CO \qquad (1)$$
$$2\ MO + C = 2\ M + CO_2 \qquad (2)$$

The experimental results showed that the malonates of Mn and Zn which have large negative values of ΔG_f of MO produced the metal oxides, and the malonates of Ni and Cu which have small negative values of ΔG_f produced the metals, and the malonates of Fe and Co which have the medium values produced the metal oxides once and then the metals by Reaction (2). Reaction (2) is considered to depend on the partial pressure of CO_2. In fact, Reaction (2) for Fe malonate did not occur in carbon dioxide. Although Reaction (2) for Co malonate occurred even in carbon dioxide, the reaction temperature was somewhat higher than that in nitrogen and an increase in weight, probably, due to re-oxidation of Co to CoO was subsequently followed.

The decomposition residues in nitrogen and in carbon dioxide contained some elementary carbon, of which the amount, in general, was found to be smaller than those in the case of the corresponding succinates which have two methylene groups. The amount of carbon seems to depend somewhat on ΔG_f of MO and on the reaction scheme, although a further investigation of many other metals is necessary to clarify these dependences.

The disproportionation of carbon dioxide represented by Reaction (3) is thermodynamically favorable, but Buttress et al.[5] found in the study of the thermal decomposition of uranyl oxalate in nitrogen that, at a temperature below 970 K,

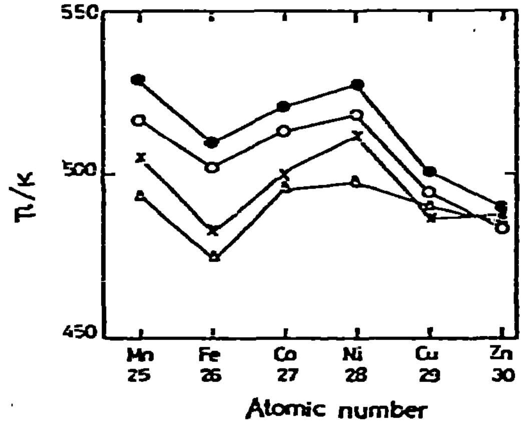


Fig. 5. Relation between initial decomposition temperature (T_i) of anhydrous transition metal malonates and atomic number. ○, in N_2; ●, in CO_2; △, in O_2; and ×, in air.

the rate of the disproportionation is very low and even on the metal oxide catalysts, there is little reaction below 770 K^6. It may be suggested, therefore, that most of the C and CO_2 formed were produced directly from the decomposition of the salts.

$$2\,CO \rightarrow CO_2 + C \tag{3}$$

Effects of ambient atmosphere on decomposition temperatures

Figure 5 shows the plots of the initial decomposition temperatures of the malonates against atomic number in various atmospheres. It was found that T_i decreased in the order of carbon dioxide, nitrogen, air and oxygen for all the salts except for Zn malonate, in the case of which the variance was small in comparison with possible experimental error. It is expected from the rule of chemical equilibrium that the decomposition reactions are depressed in carbon dioxide^7, because the main gaseous product was found to be CO_2. The reason for the accelerating effect of oxygen on the decomposition is not yet clear. However, oxygen is well known to react violently and exothermally with carbon monoxide formed by the decomposition, which leads to elevating the temperature of a part of the sample and removing carbon monoxide from the surface of the sample. These effects of oxygen seem to decrease the decomposition temperature.

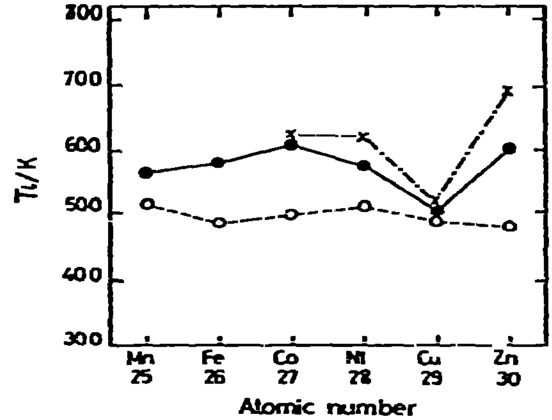


Fig. 6. Plots of T_i of anhydrous bivalent metal dicarboxylates against atomic number. ●, oxalate; O, malonate; and ×, succinate.

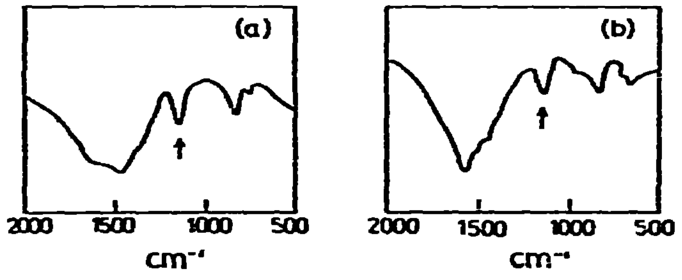


Fig. 7. Infrared spectra (KBr disk) of the products at the initial decomposition stage in carbon dioxide. (a) Mn malonate; (b) Zn malonate.

The T_i variances with the metals are the same in all the atmospheres as seen in Fig. 5, which may siggest that the decomposition of each malonate is initiated by a similar process in all the atmospheres used.

Decomposition mechanism of metal malonates

The thermal stabilities which were evaluated from T_i values, were compared among the oxalates, malonates and succinates. As is shown in Fig. 6, it was found that the malonates decompose at the lowest temperatures among the corresponding three dicarboxylates and that the variance of T_i with the metals for the malonates is considerably small compared with those for the other dicarboxylates, i.e., the metals make a poor contribution to the initiation of the decomposition in the case of the malonates. The plots of T_i of the malonates against ΔG_f of MO did not show a particular relation, which is different with the cases for oxalates[8] and succinates[2] of which the decomposition mechanisms have been described in the previous papers.

Shishido and Ogasawara[9] proposed a decomposition mechanism for alkali and alkaline earth metal malonates. The mechanism is based on the fact that a hydrogen atom in the methylene group which lies between two electron-attracting carboxyl groups behaves as a proton, which possibly brings about the decarbonation and the formation of the peculiar intermediate including the C $=$ C bond.

We found that Mn and Zn malonates release 1/3–1/2 CO_2 at the initial decomposition stages and that the products at this stage give the infrared spectra indicating the formation of the C $=$ C bond, which is well-known to show an characteristic band around 1200 cm^{-1}. The spectra of the intermediates for Mn and Zn malonates are given in Fig. 7. The results obtained in the present study do not seem to be contradictory to the mechanism proposed by Shishido and Ogasawara.

Increase in weight after complete decomposition

After the complete decomposition for Fe, Co and Ni malonates in nitrogen, a distinct increase in weight was observed in the range of 830–1300, 960–1300 and 960–1300 K, respectively, as can be seen on the TG curves in Fig. 1. A similar behavior was observed more distinctly on the decomposition of Co, Ni and Cu malonates in carbon dioxide (Fig. 2). These phenomena could not be seen on the decomposition in oxygen and in the air. This behavior scarcely appeared in the literature on the decomposition of metal carboxylates. It would be possible to assume that a trace of oxygen in nitrogen and in carbon dioxide, which were used as a flowing gas, oxidized the produced metals or that carbon dioxide itself oxidized the produced metals, because the metals produced showed such a strong pyropholicity as they burned in the air even near room temperature. The increase in weight needs to be investigated further.

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