Thermal Dehydration Reactions of Bivalent Transition Metal Malonate Dihydrates in Solid State

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The kinetics of the thermal dehydration reactions of $MC_3H_2O_4 \cdot 2H_2O$(M=Mn(II), Fe(II), Co(II), Ni(II), and Zn(II)) were studied by the Freeman-Carroll and Coats-Redfern methods on the basis of the TG and DTG in nitrogen. The most reasonable reaction order for all the salts was found to be 2/3, indicating that the rate is controlled by the chemical process at a phase-boundary. This was also confirmed by the microscopic observations. The values of activation energy and frequency factor were 70—90 kJ mol^{-1} and 10^7—10^{10} s^{-1}, respectively. The enthalpy changes for all the salts were determined to be 60—80 kJ mol^{-1} by the DSC measurements. The X-ray powder diffractograms, infrared absorption and diffuse reflectance spectra of the hydrates and anhydrous salts were also examined to obtain informations on their crystal and bonding structures.

The thermal elimination reactions of the salts containing volatile ligands such as water, ammonia and pyridine have been extensively investigated both kinetically and calorimetrically in connection with the strengths of metal-volatile ligand bonds and with the structural changes caused by the eliminations.

Most metal dicarboxylates crystallize as hydrates. Oxalates of bivalent transition metals, in many cases, contain two water molecules, which were found by the X-ray analyses to be coordinated to the metals.[1] One of water molecules in copper succinate dihydrate was found by the X-ray analysis[2] to be coordinated to the metal and it was predicted that the water molecules in the succinates of other metals are also coordinated to the metals.[3] As for the malonates investigated in this study, each of them contains two water molecules, and some preliminary experiments indicate that both of them are coordinated to the metals, so that it may be possible to characterize their dehydration reactions by appropriate kinetic and calorimetric parameters related to the strength of metal–OH_2 bonds.

Several studies dealing with the thermal dehydration reactions of metal malonates have been reported in recent years: Yttrium and scandium malonate hydrates[4] lose all of their water almost continuously, while lanthanum,[4] europium[5] and uranyl[6] malonate hydrates lose water molecules into two steps. Sodium,[7] iron,[8] nickel,[9] cobalt[10] and barium[7] malonate hydrates lose their 1, 2, 2, 2, and 0.8 moles of water in one step, while potassium malonate hydrate[7] loses one mole of water at 323—363 K and another one mole at 423—463 K. Although thermal dehydration of copper malonate trihydrate or tetrahydrate has been investigated by several workers,[11] the results are divergent, since the dehydration is followed immediately by the decomposition of its anhydrous salt.

Experimental

Materials. To prepare each of the malonates investigated, the corresponding metal carbonate was dissolved into an aqueous solution of malonic acid (10% excess) at 343 K. Precipitation of the malonate crystals occurred immediately; after the solution was allowed to stand overnight at room temperature, the crystals were filtered, washed with water, ethanol and ether, dried in air, and sieved (Tyler mesh size: 170—200) before use. The results of the elemental analyses for C, H, and metal are given in Table 1.

Table 1. Analytical data for metal malonate dihydrates

M	C(%)		H(%)		Metal(%)	
	Found	Calcd[a]	Found	Calcd[a]	Found	Calcd[a]
Mn	18.65	18.67	3.12	3.13	28.42	28.46
Fe	18.81	18.58	3.19	3.12	28.70	28.46
Co	18.23	18.29	3.01	3.07	29.76	29.91
Ni	18.29	18.31	3.07	3.07	29.81	29.83
Zn	17.83	17.71	2.98	2.97	32.03	32.13

a) Calculated for $MC_3H_2O_4 \cdot 2H_2O$ (M=metal).

Measurements. The Mössbauer spectrum of the iron salt was measured with a constant acceleration spectrometer equipped with a 400 channel pulse-height analyzer (Elron, Oxford). The lines of the sample appeared at about 0.5 and 2.3 mm s^{-1}, offering the evidence for bivalent iron.

The crystal and bonding structures of the hydrates and anhydrous salts were examined by X-ray diffraction analysis and infrared and reflectance spectroscopy. The X-ray diffractograms were obtained with a Rigaku Denki diffractometer DS, using Cu$K\alpha$ or Fe$K\alpha$ radiations. The infrared measurements were made in a frequency region of 4000—250 cm^{-1} with a Hitachi 215 spectrophotometer by the KBr disk method. The diffuse reflectance spectra in the visible region were measured with a Hitachi EPS-3T spectrophotometer equipped with a standard integrating sphere attachment.

Non-isothermal kinetic measurements were made using a Shinku Riko TGD-3000 differential thermal microbalance. Samples of about 15 mg were heated at a scanning rate of 0.083 K s^{-1} (5 K min^{-1}) under nitrogen stream with a flow rate of 1 ml s^{-1}.

A Rigaku Denki DSC-8002 differential scanning calorimeter, calibrated by the heat of transition of KNO_3 (ΔH= 51.3 kJ mol^{-1} at 401 K), was used for the heat measurements. The details of experimental conditions were described previously.[12]

Kinetic Procedures. The values of reaction order (n) and activation energy (E_a) were found graphically using the Freeman-Carroll method[13]

$$\frac{-E_a/2.3R\,\Delta\left(\frac{1}{T}\right)}{\Delta \log (W-W_c)} = -n + \frac{\Delta \log \frac{dW}{dt}}{\Delta \log (W-W_c)}$$

where W=sample weight at temperature T; W_c=sample weight at the completion of reaction; dW/dt=the rate of change in sample weight at temperature T. The values of $(W-W_c)$ and dW/dt were determined directly from TG and DTG curves, respectively, in terms of 15—20 divisions.

The frequency factor (A) was calculated using the basic relation:

$$\frac{d\alpha}{dt} = Ae^{-E_a/RT}(1-\alpha)^n$$

where α means the degree of reaction, $(W_0-W)/(W_0-W_c)$ (W_0=initial sample weight).

The values of E_a and n obtained using the Freeman-Carroll method were checked by the Coats-Redfern method[14] which allows a good linearization if the correct n value is assumed:

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log\frac{AR}{\phi E_a}\left[1-\frac{2RT}{E_a}\right] - \frac{E_a}{2.3RT}$$

where ϕ means heating rate.

Results and Discussion

Dihydrates. Recently, the diffraction and crystallographic data of several malonates have been reported;[8,10,15] according to them, the crystals of manganese and iron malonate dihydrates belong to the orthorhombic system, and those of cobalt, nickel and zinc to the monoclinic system. The authors have also obtained the X-ray diffractograms of all these salts, together with their infrared absorption spectra given in Fig. 1. The salts of the same crystal system give similar spectra, whereas there are apparant differences between the spectral pattern of the salts of the orthorhombic system and that of the salts of the monoclinic system. Most of absorptions can be assigned easily by applying the bands assignments made successfully with sodium malonate,[16] but two absorptions in the region of 900—850 cm^{-1}, observed only with the salts of Co, Ni and Zn (monoclinic system), could not be assigned. Sodium malonate, malonic acid and di- or tri-malonato complexes do not show any absorption in this region.[16] Some particular bonding manner may exist in these salts.

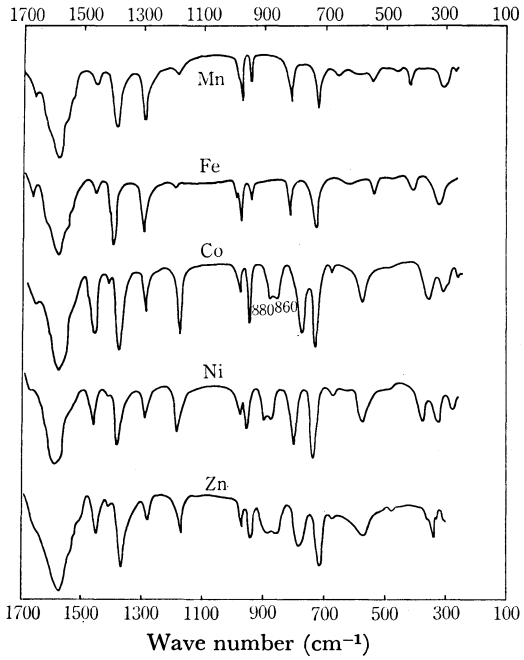

Fig. 1. Infrared absorption spectra of metal malonate dihydrates.

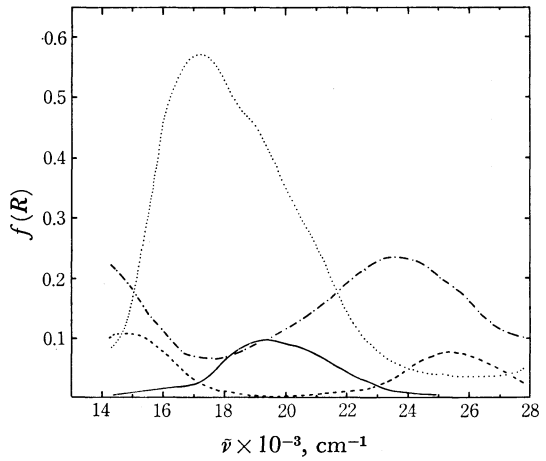

Fig. 2. Reflectance spectra of malonate dihydrates and anhydrous malonates. ——: $CoC_3H_2O_4\cdot 2H_2O$, ……: $CoC_3H_2O_4$, ----: $NiC_3H_2O_4\cdot 2H_2O$, -·-·-: $NiC_3H_2O_4$.

The diffuse reflectance spectra of the cobalt and nickel salts in Fig. 2 indicate that each metal is surrounded octahedrally by six oxygen atoms.[17] Since a malonate ion has four oxygen atoms, two water molecules of $MC_3H_2O_4\cdot 2H_2O$ (M=Co and Ni) seem to be coordinated to the metals.

Dehydration Reactions. The TG, DTA, DTG, and DSC curves were obtained in a nitrogen atmosphere for all the salts investigated. All the curves corresponding to the dehydration were smooth so that the dehydration reactions seems to take place in one step. The initial weight-loss temperatures (T_i), weight-loss values (W_0-W_c) and peak temperatures of DTG (T_m) are given in Table 2. The weight-loss data confirm the formura $MC_3H_2O_4\cdot 2H_2O$. Both T_i and T_m vary considerably with the metals and the variations are similar to those of metal oxalate dihydrates in which two water molecules are coordinated to the metals. Moreover, T_i, and T_m of the malonates are relatively higher than the ordinary values for the elimination of crystalline water. These facts support the view that

Table 2. Initial weight-loss temperatures (T_i), DTG peak temperatures (T_m) and weight-loss values (W_0-W_c) for the reaction

$MC_3H_2O_4\cdot 2H_2O(s) \rightarrow MC_3H_2O_4(s)+2H_2O(g)$

M	T_i/K	T_m/K	$(W_0-W_c)_{obsd}$ (%)	$(W_0-W_c)_{calcd}$ (%)
Mn	393	453	18.4	18.7
Fe	392	456	17.4	18.6
Co	396	456	17.1	18.3
Ni	430	501	19.7	18.3
Zn	342	395	16.8	17.7

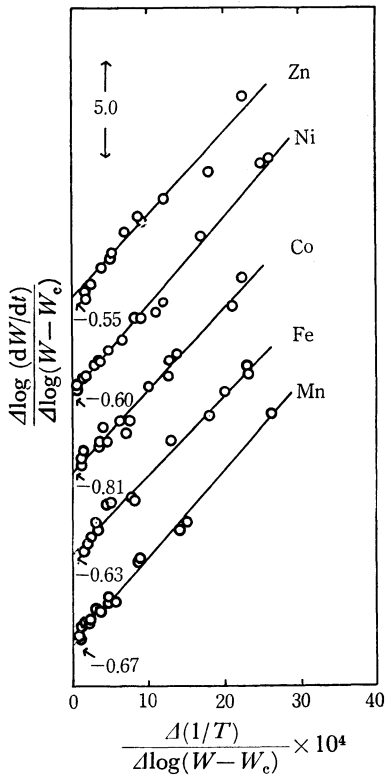

Fig. 3. Plots by the Freeman-Carroll method.

TABLE 3. REACTION ORDERS (n), ACTIVATION ENERGIES (E_a), FREQUENCY FACTORS (A) AND ENTHALPY CHANGES (ΔH) FOR THE REACTION

$MC_3H_2O_4\cdot 2H_2O(s) \rightarrow MC_3H_2O_4(s)+2H_2O(g)$

M	n	E_a/KJ·mol^{-1} F-C[a]	E_a/KJ·mol^{-1} C-R[b]	A/s^{-1}	ΔH/ KJ·mol^{-1}
Mn	0.67±0.23	88.6±4.2	86.9	5.2×10^9	73.6
Fe	0.63±0.19	80.7±2.9	76.9	2.3×10^7	65.6
Co	0.81±0.21	83.6±3.8	76.5	3.6×10^8	77.3
Ni	0.60±0.13	92.0±2.5	80.7	4.2×10^7	77.7
Zn	0.55±0.14	80.7±4.2	76.5	4.3×10^9	69.4

a) Freeman-Carroll method. b) Coats-Redfern method.

the water molecules in all the malonates are also coordinated.

The kinetic analyses of the traces of the TG and DTG curves lead to the plots shown in Fig. 3, yielding the values of activation energy and reaction order given in Table 3 (Freeman-Carroll method). For all the salts, a reaction order of 2/3 was found to fit best the experimental results, indicating that the dehydration begins on the surface of the crystals and propagates uniformly to their centers. Consequently it is probable that the overall reaction rate is controlled by the chemical process at the phase-boundary formed by the reactant and the product.

Figure 4 shows the microscopic photographs of partially dehydrated manganese malonate heated up to 434 K in nitrogen, indicating that the reaction proceeds from the outer surface of each particle inwards. The crystalline hydrate became finally amorphous on dehydration. As shown in Fig. 5, the change of the X-ray powder diffraction patterns for the manganese salt correspond well to the microscopic observations. Other anhydrous salts were also found to be amorphous to X-rays, supporting the former reports on iron[8] and cobalt[9] salts.

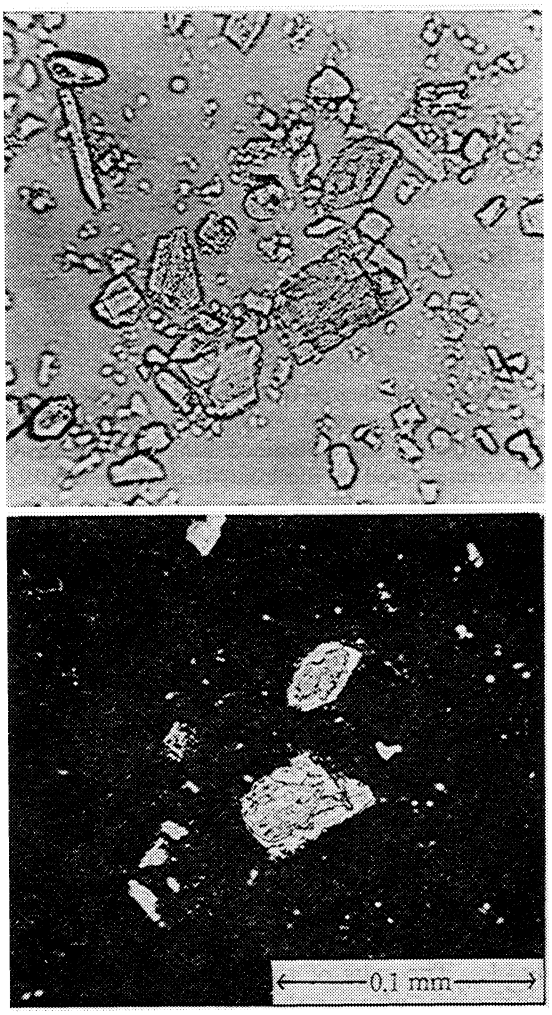

Fig. 4. Microscopic photographs of partially dehydrated manganese malonate; the lower one was taken between crossed polarizers.

When n is assumed to be 2/3, the plots by the Coats-Redfern method give good straight lines to yield E_a given in Table 3. The values agreed with those obtained by the Freeman-Carroll method, although the former values are somewhat lower. The bond strength of M–OH_2 is expected to be a function of the size of the metal ion if electrostatic attraction between it and the oxygen lone-pair is assumed, or to follow the well-known Irving-Williams order if ligand field effect is taken into consideration; but the variation of E_a in Table 3 with the metals are not as expected and the value for the manganese salt is apparently quite high. The bond strengths of M–OH_2 thus seem to be better reflected on T_i (or T_m) rather than on E_a.

The heat changes caused by the dehydration are given in Table 3. These values correspond to the average enthalpy changes per one mole of H_2O. Since the enthalpy changes obtained involve the amount corresponding to the change in the physical state of

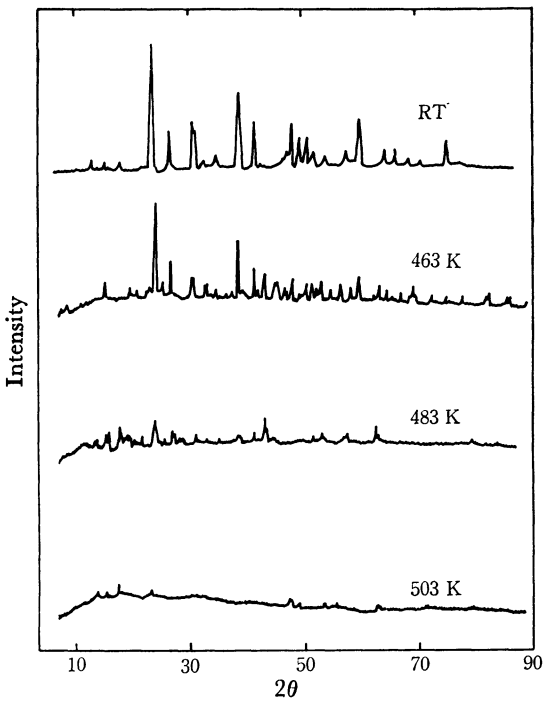

Fig. 5. X-Ray diffraction patterns of manganese malonate dihydrate and its dehydration products heated at various temperatures.

H_2O (ΔH_w), the net increases of enthalpy caused by dehydration may be 10—30 KJ mol^{-1} if ΔH_w is assumed to be in the vicinity of the heat of sublimation of ice (52 KJ mol^{-1}).

With a few exceptions, the ΔH of the malonates tends to increase with the increase of E_a, as shown in many elimination reactions. There are also remarkable differences in ΔH between the malonates and the oxalates.[18] The value for a malonate is always 10—20 KJ mol^{-1} larger than that for the corresponding oxalate. Since the values of T_i, which is seemingly a measure of the bond strengths of M–OH_2, are not so much different between the malonates and the oxalates, the differences in ΔH may be due to other factors. Other differences between these two carboxylates observed during dehydration are as follows: (1) all of the anhydrous malonates give broad infrared absorption bands, whereas anhydrous oxalates (as well as all the hydrates) give narrow bands; (2) the anhydrous malonates are poorer than the anhydrous oxalates in their crystallinity; (3) in the case of colored salts, the dehydration of the malonates are accompanied with more drastic color changes than that of the oxalates (*cf.* Table 4). These observations suggest that, compared with the anhydrous oxalates, the anhydrous malonates are composed of networks of more loosely linked polymers with higher potential energy.

Table 4. Color and spectral changes accompanying dehydration of malonate and oxalate dihydrates

Compound	Color	$\bar{\nu}_{max}/cm^{-1}$
Co(mal)·$2H_2O$	pink→bluish violet	19400→17100
Ni(mal)·$2H_2O$	greenish blue→yellow	25400→23500
Co(ox)·$2H_2O$	pink→reddish violet	19200—20400→19900
Ni(ox)·$2H_2O$	blue→yellowish green	27100→25700

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