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Thermal Dehydration and Decomposition Reactions of Bivalent Metal Oxalates in the Solid State

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The thermal dehydration and decomposition of the oxalates of Mg(II), Ca(II), Sr(II), Ba(II), Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) were investigated by means of TG, DTA, DSC, EGA, X-ray powder diffraction analysis, and reflectance and infrared spectroscopies. In general, the temperature at which the oxalates were dehydrated increased with $1/r$, where r denotes the radius of metal ion. The heats of dehydration(ΔH_{H_2O}) of the alkaline earth metal oxalates increased with $1/r$, but those of transition metal oxalates decreased as $1/r$ increased. By considering the decomposition products, the reactions of anhydrous oxalates were classified into three groups and the relations between the decomposition temperatures and $1/r$ were discussed for each group.

The thermal decomposition reactions of metal oxalates have been extensively investigated. The thermographic curves of a number of metal oxalates have been described by Ugai[1] and many other researchers. Dollimore and his co-workers[2–4] measured changes in length or volume of samples subjected to heat treatment, or surface-area changes occurring on dehydration, and discussed the effect of dehydration on the subsequent decompositions. Lagier and his co-workers[5–7] found that, for the oxalates of Mg, Mn, Fe, Co and Zn, at least two phases of the compounds exist and that the phases observed depended on the method of preparation. They studied the dependence of dehydration of $CoC_2O_4 \cdot 2H_2O$ on the differences of the two phases. Kinetic studies on the dehydration and decomposition of a number of oxalates were carried out by isothermal and temperature elevation methods. In many cases, however, the parameters reported by each researcher for a given oxalate were different.

In the present paper, the thermal dehydration and decomposition reactions of bivalent metal oxalates were systematically discussed on the basis of the relations between the nature of the metal ions and the initial weight-loss temperatures or enthalpy changes.

Experimental

Materials. The oxalates of alkaline earth metals and transition metals investigated were precipitated with alkali oxalates (or oxalic acid) from solutions of soluble salts of the corresponding metals, washed thoroughly with water and dried in air. The elemental analyses for C and H agreed with the calculated values within ±0.3%.

Measurements. Thermogravimetric (TG) and differential thermal analytic (DTA) curves were obtained with a Shinku Riko TGD-3000 at a heating rate of 5 °C/min in an atmosphere of nitrogen flowing at 50 ml/min. About twenty milligrams of powdered sample in a platinum crucible were used for each measurement. Differential scanning calorimetric (DSC) curves were recorded with a Rigaku Denki 8002 CS at a heating rate of 5 °C/min in an atmosphere of nitrogen flowing at 30 ml/min. About twenty milligrams of powdered sample were placed in a crucible made from 0.1 mm thick aluminum sheet. A lid of the same material was placed inside the crucible. The reference material was α-Al_2O_3. The instrument was calibrated against the heat of the transition of KNO_3 which appears at 128 °C with ΔH equal to 12.28 kcal/mol.

High temperature X-ray diffractions were measured in an atmosphere of nitrogen flowing at 30 ml/min with a Toshiba ADG–101 diffractometer equipped with a standard high temperature sample holder. Cu$K\alpha$ radiation and a nickel filter were used in all measurements. Infrared absorption spectra were measured from 2500 to 400 cm^{-1} in KBr disks with a Hitachi EPI–3G spectrophotometer. The sample was heated under conditions identical to those for the TG measurements. When the temperature of the sample reached the desired value, heating was stopped, the sample was cooled to room temperature and its infrared absorption spectrum was recorded. Diffuse reflectance spectra were measured with a Hitachi EPS–3T spectrophotometer equipped with a standard integrating sphere attachment. MgO was used as the reference material. The heated sample was treated in the same way as for the measurement of the infrared spectra.

Evolved gas (EG) curves were obtained using a conductometric technique. The evolved gas analyses (EGA) were carried out using an activated charcoal column (2 meters long) and a helium carrier gas (50 ml/min). In both cases the procedures described in a previous paper[8] were employed.

Results

TG and DTA curves in the temperature range from room temperature to 1000 °C in a flowing nitrogen atmosphere are given in Figs. 1 and 2. The thermal data obtained are summarized in Table 1 together with the radii of the metal ions (Goldschmidt's crystallographic radii). The TG curve of $CaC_2O_4 \cdot H_2O$ shows that the decomposition took place at three stages, as indicated in previous paper.[1] On the DTA curve, a small exothermic peak, which has not been previously reported, was observed at 290 °C without any weight-loss. $SrC_2O_4 \cdot 2H_2O$ decomposed to $SrCO_3$ after dehydration; $SrCO_3$ did not decompose further, but the γ-$SrCO_3$ to β-$SrCO_3$ phase transition was observed at 875 °C. The DTA curve for $SrC_2O_4 \cdot 2H_2O$ also had an exothermic peak at 259 °C which was more prominent than that of $CaC_2O_4 \cdot H_2O$. This change without weight-loss was not reversible (*i.e.* not reflected on the cooling curve), indicating that the lower-temperature form is metastable with respect to the higher-temperature one. The X-ray powder diffraction patterns showed that this change corresponds to recrystallization of poorly crystalline SrC_2O_4 formed

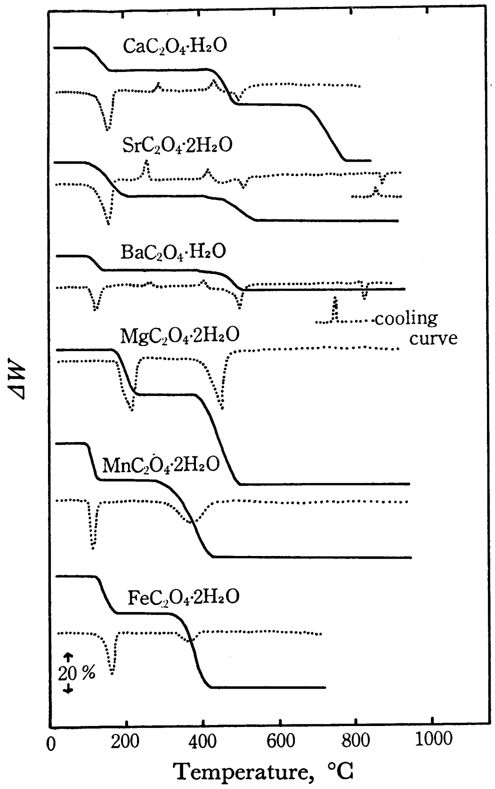

Fig. 1. TG (solid line) and DTA (dotted line) curves of metal oxalates in a flowing nitrogen atmosphere.

on dehydration. The heat of this process was found to be 3.2 kcal/mol by DSC. The TG and DTA curves of $BaC_2O_4 \cdot H_2O$ were very similar to those of $SrC_2O_4 \cdot 2H_2O$.

The oxalates containing metal ions with radii smaller than that of calcium ion decomposed to metal oxides or metals. The oxalates of Mg, Mn, Fe and Zn decomposed at lower temperatures as the radius of the metal ion increased and formed the metal oxides and an equimolar mixture of CO and CO_2, whereas the oxalates of Co, Ni and Cu decomposed at higher temperatures as the metal ion radius increased, and gave the metals and CO_2.

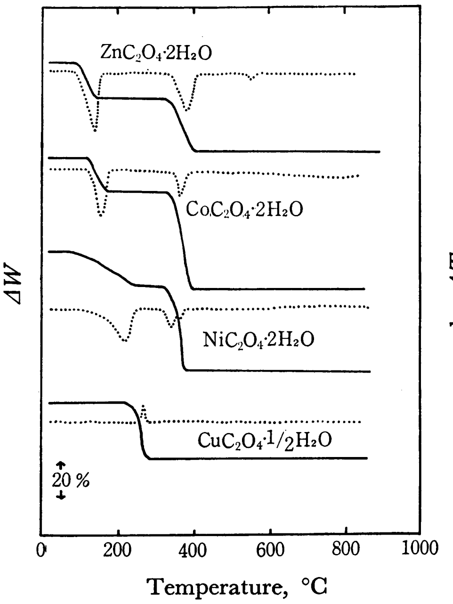

Fig. 2. TG (solid line) and DTA (dotted line) curves of metal oxalates in a flowing nitrogen atmosphere.

The reactions of the oxalates investigated may be expressed as,

$$MC_2O_4 \rightarrow MCO_3 + CO,$$
$$\text{where } M = Ca(II),\ Sr(II) \text{ and } Ba(II) \tag{1}$$
$$MC_2O_4 \rightarrow MO + CO + CO_2,$$
$$\text{where } M = Mg(II),\ Mn(II),\ Fe(II) \text{ and } Zn(II) \tag{2}$$
$$MC_2O_4 \rightarrow M + 2CO_2,$$
$$\text{where } M = Co(II),\ Ni(II) \text{ and } Cu(II) \tag{3}$$

These stoichiometries were confirmed by analyses of gaseous products, *cf.* Table 2.

The heats of dehydration (ΔH_{H_2O}) and of decomposition (ΔH_d) were measured by DSC. The results are given in Table 3. The values of ΔH_{H_2O} of alkaline earth metal oxalates increased almost parallel to the increase of the initial weight-loss temperatures(t_{H_2O}), while ΔH_{H_2O} of transition metal oxalates decreased with increasing t_{H_2O}. For decomposition of the an-

TABLE 1. THERMAL ANALYSES AND RADII OF METAL IONS

Compound	Dehydration			Decomposition of anhydrous oxalate				Radius of metal ion/Å
	$t^a_{H_2O}$/°C	Weight-loss/%		t_d $^{b)}$/°C	Product	Weight-loss/%		
		obsd	calcd			obsd	calcd	
$MgC_2O_4 \cdot 2H_2O$	157	23.6	24.3	380	MgO	46.4	48.5	0.78
$CaC_2O_4 \cdot H_2O$	100	12.5	12.3	418	$CaCO_3$	19.1	19.2	0.99
$SrC_2O_4 \cdot 2H_2O$	93	16.8	17.0	403	$SrCO_3$	14.0	13.2	1.27
$BaC_2O_4 \cdot H_2O$	97	6.2	7.4	395	$BaCO_3$	10.3	11.5	1.43
$MnC_2O_4 \cdot 2H_2O$	95	20.5	20.1	290	MnO	41.6	40.2	0.91
$FeC_2O_4 \cdot 2H_2O$	116	20.2	20.0	310	FeO	39.9	40.0	0.83
$CoC_2O_4 \cdot 2H_2O$	118	21.0	19.7	338	Co	47.0	48.1	0.82
$NiC_2O_4 \cdot 2H_2O$	137	18.6	19.7	310	Ni	46.7	48.2	0.78
$CuC_2O_4 \cdot 1/2H_2O$	—	—	—	235	Cu	59.8	60.2	0.72
$ZnC_2O_4 \cdot 2H_2O$	92	18.7	19.0	329	ZnO	39.3	38.0	0.83

a) Initial weight-loss temperature of dehydration. b) Initial weight-loss temperature of decomposition.

Table 2. Analyses of gaseous products of the anhydrous oxalates by EGA

Compound	Analysis temp./°C	Evolved gas (mol%)
MnC_2O_4	360	CO(48), CO_2(52)
FeC_2O_4	355	CO(44), CO_2(56)
CoC_2O_4	350	CO(17), CO_2(83)
NiC_2O_4	310	CO(0), CO_2(100)
CuC_2O_4	240	CO(0), CO_2(100)
ZnC_2O_4	350	CO(46), CO_2(54)

Table 3. Heat of the dehydration(ΔH_{H_2O}) and heat of decomposition(ΔH_d) of the metal oxalates determined by DSC

Compound	ΔH_{H_2O}/kcal per 1 mol of H_2O	ΔH_d/kcal per 1 mol of oxalate
$MgC_2O_4\cdot 2H_2O$	15.4	24.7
$CaC_2O_4\cdot H_2O$	15.1	—
$SrC_2O_4\cdot 2H_2O$	10.9	—
$BaC_2O_4\cdot H_2O$	11.2	—
$MnC_2O_4\cdot 2H_2O$	16.1	16.4
$FeC_2O_4\cdot 2H_2O$	14.9	7.3
$CoC_2O_4\cdot 2H_2O$	13.7	8.6
$NiC_2O_4\cdot 2H_2O$	13.2	9.3
$CuC_2O_4\cdot 1/2H_2O$	—	—
$ZnC_2O_4\cdot 2H_2O$	15.1	19.6

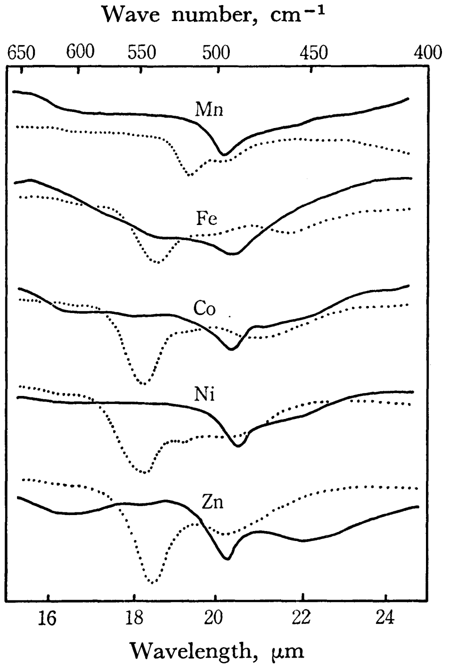

Fig. 3. Infrared absorption spectra of metal oxalates before and after dehydration.
——: $MC_2O_4\cdot 2H_2O$, ····: MC_2O_4.

hydrous oxalates, the values of ΔH_d of the oxalates which gave metal oxides or metals as decomposition products had no particular relation to the initial weight-loss temperatures (t_d). The values of ΔH_d of oxalates which gave the corresponding metal carbonates could not be measured accurately.

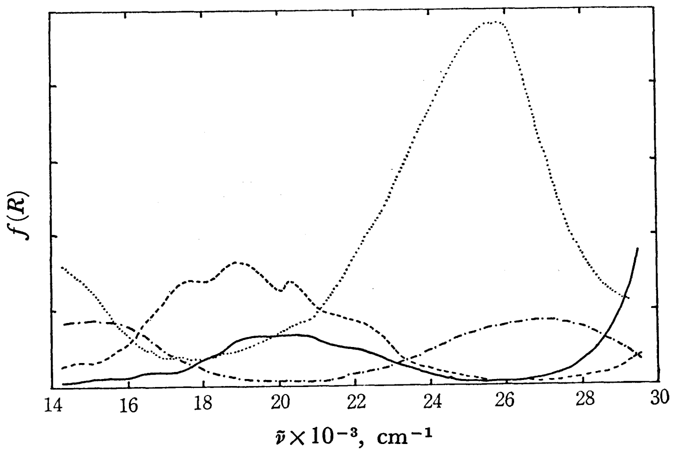

Fig. 4. Reflectance spectra of $CoC_2O_4\cdot 2H_2O$, $NiC_2O_4\cdot 2H_2O$ and their anhydrous compounds.
——: $CoC_2O_4\cdot 2H_2O$, ----: CoC_2O_4, -·-: NiC_2O_4, ····: NiC_2O_4.

The infrared absorption spectra were measured before and after the dehydration. In the region from 2500 to 650 cm^{-1}, the spectra of the anhydrous oxalates were almost the same as those of the hydrated oxalates, whereas in the region of 650 to 400 cm^{-1}, considerable differences were observed between MC_2O_4 and $MC_2O_4\cdot 2H_2O$ as shown in Fig. 3. The peaks near 500 cm^{-1} which were attributed mainly to ν(M–O (ox)) were shifted to higher frequencies by the removal of water molecules, where O(ox) represents an oxygen atom of oxalate ion. On dehydration, the color of $CoC_2O_4\cdot 2H_2O$ changed from pink to purple and that of $NiC_2O_4\cdot 2H_2O$ from bluish green to yellowish green. The reflectance spectra in the visible region of both the oxalates which were measured before and after the dehydration are given in Fig. 4. The d–d transition bands shifted slightly to lower frequencies and the value of $f(R)$ increased on dehydration, where R denotes the reflectance and $f(R)$ the Kubelka-Munk function, $f(R)=(1-R)^2/(2R)$.

Discussion

From X-ray analysis, structure of $MC_2O_4\cdot 2H_2O$ has been reported to be as shown in Fig. 5, where the oxalate ions act as a quadridentate ligand and the water molecules coordinate directly to the metal ions.[5] Therefore, t_{H_2O} and ΔH_{H_2O} are considered to reflect the nature of the metal ions.

The values of t_{H_2O} in Table 1 give information about the dissociation energy of M–OH$_2$. On the other hand, it is supposed that, since the water molecules are bonded to the metal ions by electrostatic forces, the

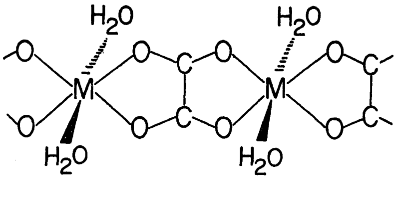

Fig. 5. Bonding structure of $MC_2O_4\cdot 2H_2O$.[5]

bond energy is a function of the size of metal ion. Therefore, the observation that t_{H_2O} increases with $1/r$, as seen in Table 1, seems to be reasonable. The bond energy of M–OH_2 may be estimated from the value of ν(M–O(ox)), since it seems that the more strongly the water molecules are bonded to the metal ion, the weaker the M–O(ox) bond is. On this basis, the experimental results, which are given in Fig. 3, suggest that the bond energies of M–OH_2 increase in the order: Mn<Zn<Fe<Co<Ni. Therefore, the results obtained from the thermal studies are consistent with those from infrared absorption spectra.

The heat of dehydration (ΔH_{H_2O}) gives the difference in potential energy between the hydrated and anhydrous oxalates. In the transition metal group the values of ΔH_{H_2O} decreased almost parallel with the increase in $1/r$. This indicates that the increase of the potential energy on the dissociation of M–OH_2 is somewhat cancelled by an increase in the bond energy of M–O(ox). In fact, the increase of the bond energies of M–O(ox) on removing the coordinated water molecules increased in the order: Mn<Zn<Fe<Co<Ni (*cf.* Fig. 3). The frequency shifts for ν(M–O(ox) were as follows: Mn, 23; Zn, 45; Fe, 48; Co, 55; Ni, 63 cm^{-1}. In the case of the alkaline earth metal oxalates, the oxalates of Mg(II) and Sr(II) each contain two water molecules, while those of Ca(II) and Ba(II) each contain one water molecule. Therefore, a systematic interpretation similar to that made the transition metal oxalates may not be possible.

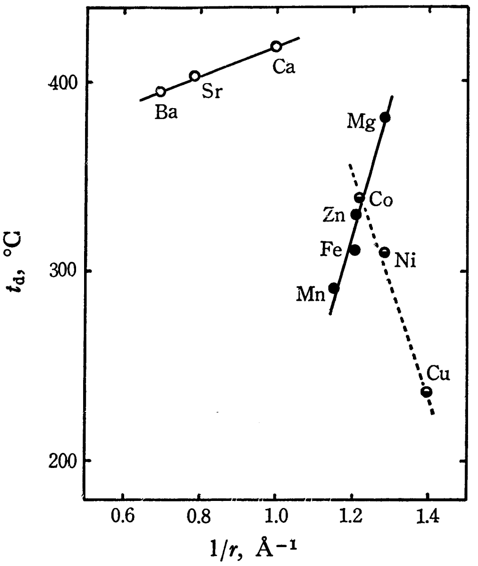

Fig. 6. Relation of initial weight-loss temperatures of the decomposition (t_d) with $1/r$.
○: $MC_2O_4 \rightarrow MCO_3+CO$, ●: $MC_2O_4 \rightarrow MO+CO+CO_2$, ◒: $MC_2O_4 \rightarrow M+2CO_2$.

The relation of the initial weight-loss temperature of for the decomposition (t_d) to $1/r$ depends on the decomposition mechanism as seen in Fig. 6. The M–O (ox) bond energies in the anhydrous oxalates are considered to be the larger, the smaller the complexed metal ions are. Therefore, decomposition of the oxalates to the metal oxides may be initiated by M–O (ox) bond breaking, since these oxalates decomposed at higher temperatures as $1/r$ increased. On the other hand, the oxalates of Co, Ni and Cu, which decompose at lower temperatures as $1/r$ increases, may decompose by electron transfer from the oxalate ion to the metal ions. This is supported by the fact that the electron affinities of metal ions, in general, increase with increasing effective ionic charge.

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